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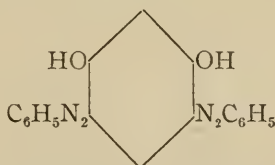
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[Contributions from the Chemical Laboratory of Cornell University.]

## SOME DISAZO AND TRISAZO DERIVATIVES OF RESORCIN.

BY W. R. ORNDORFF AND B. J. RAY.

It is a well-known fact that the diazonium salts combine with resorcin to give two isomeric disazo compounds. One of these, known as the symmetrical resorcindisazobenzene, is formed by combining the diazonium salt with resorcin in caustic alkali solution in the proportion of two molecules of the former to one of the latter. That this substance is really the symmetrical compound,



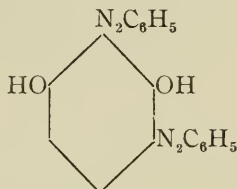
Symmetrical Resorcindisazobenzene.

follows from the work of Kostanecki,<sup>1</sup> who showed that it gives the symmetrical 4,6-diaminoresorcin on reduction with tin and hydrochloric acid. This symmetrical resorcindisazobenzene is identical with the  $\alpha$ -resorcindisazobenzene

<sup>1</sup> Ber. d. chem. Ges., **21**, 3114.

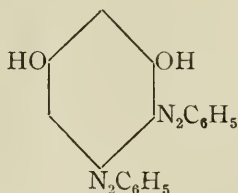
previously made by O. Wallach and B. Fischer,<sup>1</sup> as shown by the fact that both yield the same diacetyl compound melting at 183°–184°.

The second, or unsymmetrical, resorcindisazobenzene,



Unsymmetrical Resorcindisazobenzene.

was first obtained by Liebermann and Kostanecki<sup>2</sup> as a by-product in the preparation of resorcinmonazobenzene and was separated from this by means of its insolubility in dilute alkalis. As it was not identical with either the  $\alpha$  or  $\beta$  compound of Wallach and Fischer, they named it  $\gamma$ -resorcindisazobenzene. Later, Kostanecki<sup>3</sup> found that it is exclusively formed when two molecules of the diazonium salt and one of resorcin are combined in the presence of sodium acetate or sodium carbonate solutions. It yields a diacetyl compound which melts at 137°–138° and differs in other respects from the symmetrical product. That it has the unsymmetrical structure represented by the above formula was proven by the fact that on reduction with tin and hydrochloric acid it gives the unsymmetrical 2,4-diaminoresorcin.<sup>4</sup> The only other theoretically possible formula for a resorcindisazobenzene,



has an azo group in the meta position to both hydroxyl groups,

<sup>1</sup> Ber. d. chem. Ges., **15**, 2814.

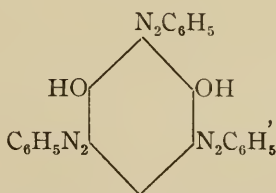
<sup>2</sup> *Ibid.*, **17**, 880.

<sup>3</sup> *Ibid.*, **21**, 3114.

<sup>4</sup> *Ibid.*, **17**, 880.

which Kostanecki<sup>1</sup> thinks is very improbable, since there are both an ortho and a para position free. In a footnote he suggests this formula for the  $\beta$ -resorcindisazobenzene of Wallach and Fischer, which is formed only in very small quantity, together with the symmetrical compound, when a caustic potash solution of the monazo product is treated with a diazonium salt. He is careful to point out, however, that, as the reduction products of this  $\beta$  compound are not known, this structural formula has no valid basis.

If the two structural formulas given above for the symmetrical and the unsymmetrical resorcindisazobenzenes be examined, it will be seen that in the symmetrical compound both azo groups have entered the molecule in the para position to one of the hydroxyl groups and ortho to the other, while in the unsymmetrical product only one of the azo groups is para to one of the hydroxyl groups and ortho to the other, the second azo group having taken the position ortho to both of the hydroxyl groups. In other words, *in each compound there is a position vacant which is occupied by an azo group in the other*. It seemed highly probable, therefore, that it would be possible to introduce azo groups into these unoccupied positions and thus make trisazo compounds of resorcin. Furthermore, both of the above disazo compounds should yield the same trisazo product when treated with benzenediazonium chloride,



Resorcin-2,4,6,-trisazobenzene.

and the positions of the azo groups would thus be determined as 2, 4 and 6, since in the symmetrical product the azo groups are known to be in positions 4 and 6 and in the unsymmetrical compound in 2 and 4. There was also the possibility that

<sup>1</sup> Ber. d. chem. Ges., 21, 3114.

the  $\beta$ -resorcindisazobenzene of Wallach and Fischer might be the above trisazo compound, as it was made by the action of benzenediazonium chloride on a solution of resorcinmonazobenzene in caustic potash, and there seems to be no reason why the symmetrical disazo compound, which is formed here in much larger quantity and is soluble in caustic potash solution, should not be, partly at least, converted into the trisazo product by the diazonium salt.

Following out this line of reasoning, we made the above trisazo compound from both the symmetrical and unsymmetrical disazo product, as well as from benzenediazonium chloride and resorcin by combining them in the proportion of three molecules of the former to one of the latter. After we had completed this work and were making other trisazo compounds of resorcin, the article on phenol-2,4,6-trisazobenzene, by E. Grandmougin and H. Freimann, appeared.<sup>1</sup> This caused us to publish a short preliminary paper on resorcin-2,4,6-trisazobenzene in the same journal.<sup>2</sup>

About this time, also, we found in the article of Wallach and Fischer<sup>3</sup> the following statement, which had previously escaped us and also, apparently, Grandmougin and Freimann, as they make no mention of it: "*Wir haben uns endlich davon überzeugt dass die Disazoverbindungen sich sehr leicht in Trisazoverbindungen überführen lassen, indem man die  $\alpha$ -Disazoverbindungen in alkalischer Lösung mit Diazoverbindungen umsetzt. Diese Trisazoverbindungen sind aber bisher noch nicht näher untersucht.*" It seems very remarkable, in view of this statement, that Wallach and Fischer never even suspected that their  $\beta$ -resorcindisazobenzene, which was made by treating the monazo compound dissolved in strong caustic potash solution with benzenediazonium chloride, was in reality nothing but an impure trisazo compound.

The only other mention in the literature of trisazo compounds of this type, in which all of the azo groups are connected with the same benzene residue, is found in an article published

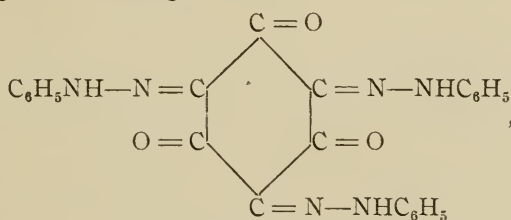
<sup>1</sup> Ber. d. chem. Ges., **40**, 2662 (1907).

<sup>2</sup> *Ibid.*, **40**, 3212 (1907).

<sup>3</sup> *Ibid.*, **15**, 2814.



in 1897 by A. G. Perkin<sup>1</sup> on phloroglucinoltrisazobenzene. This compound was made by adding an excess of a solution of benzenediazonium sulphate to a solution of phloroglucinol in dilute sodium carbonate solution. Perkin found that the formation of this trisazo product was not dependent on the amount of the diazonium salt present, as the same trisazo compound was always formed even if the disazonium salt were present in the proportion of one or two molecules to one molecule of the phloroglucinol, part of the phloroglucinol being unacted on in this case. He regards the substance as having the following structure,



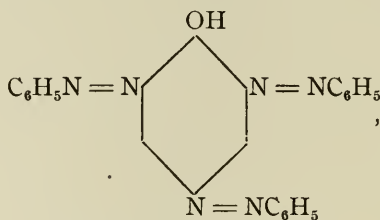
Phloroglucinoltrisazobenzene.

since "it is insoluble in cold alkali solutions and contains no hydroxyl groups, those originally present in the phloroglucinol having assumed the ketonic form from their ortho position relatively to the azo groups." This trisazo compound dissolves in concentrated sulphuric acid with a deep crimson coloration and, as was to be expected, it also results from the action of diazobenzene sulphate on an alkaline solution of phloroglucinoldisazobenzene.

Grandmougin and Freimann state that phenol-2,4,6-trisazobenzene is formed, together with phenoldisazobenzene, when three molecules of diazonium chloride act on phenol in caustic alkaline solution, and they emphasize the fact that their trisazo compounds were formed only in the presence of caustic alkalis, while in the case of monazo compounds it is a matter of indifference whether the combination be brought about with caustic alkalis or with the alkaline carbonates or acetates. In the formation of the disazo compounds of phenol, however, the presence of acetate is unfavorable to

<sup>1</sup> J. Chem. Soc., 71, 1154.

the reaction, which takes place readily in solutions of the alkaline carbonates or hydroxides. In the latter case some trisazo product may also be formed as a by-product. They give the following formula to their phenoltrisazobenzene,



Phenol-2,4,6,-trisazobenzene.

since, on reduction with tin and hydrochloric acid, it gives 2,4,6-triaminophenol identical with the reduction product of picric acid.

Freimann<sup>1</sup> gives the following generalizations in regard to the color of the azo compounds of phenol when dissolved in concentrated sulphuric acid: the monazo compounds dissolve in concentrated sulphuric acid with a pure yellow color, which remains yellow on dilution, the disazo products with a yellowish-orange color, which becomes red to dirty reddish-violet on dilution and the trisazo compounds dissolve in the same solvent with a deep reddish-violet color and are precipitated out on dilution. It will be seen that the trisazo compounds of phloroglucinol prepared by Perkin differ from the trisazo compounds of phenol in two respects. In the first place they are formed in the presence of sodium carbonate, caustic alkalies not being essential for their formation, and in the second place they dissolve in concentrated sulphuric acid with a deep crimson color.

In regard to the position and number of the azo groups which enter the phenol molecule, three cases have been distinguished up to the present time:<sup>2</sup>

1. If equimolecular quantities of the phenol and the diazonium salt react there is formed:

<sup>1</sup> Zur Kenntnis der Azo-Derivate des Phenols und der Phenolcarbonsäuren; Diss. Zürich, 1908.

<sup>2</sup> V. Meyer and P. Jacobson: Lehrbuch d. org. Chemie, II, 1, 397.

(a) From a phenol in which the para position to the hydroxyl group is unoccupied, a *parahydroxyazo* compound.

(b) From a phenol whose para position to the hydroxyl group is occupied, but whose ortho position is free, an *ortho-hydroxyazo* compound.

2. If two molecules of the diazonium salt react with one molecule of the phenol there is formed a hydroxydisazo compound, when the para position to the hydroxyl group in the phenol and at least one ortho position are free. These disazo products are also formed as by-products when equimolecular quantities react.

It has also been found that *p*-hydroxybenzoic acid reacts with diazonium salts, yielding the same products as phenol itself, owing to the elimination of carbon dioxide.<sup>1</sup> This is true also for the trisazo compounds, as Grandmougin and Freimann found that the product, melting at 213°–215°, first prepared by Limpricht and Fitze<sup>2</sup> by the action of benzene-diazonium chloride on *p*-hydroxybenzoic acid, was phenol-2,4,6-trisazobenzene. They also found that a small amount of the azo derivative of the carbonic acid is formed here.

For case (1a) the following exceptions have been observed: *o*-Hydroxyazo compounds are formed, together with the *p*-hydroxyazo products, even when the para position to the hydroxyl group is free. Thus, in the action of diazotized nitrotoluidine on nitrocresol, *o*-azonitrotoluenenitrocresol is formed as well as the para product,<sup>3</sup> and in the direct combination of a diazonium salt with phenol there is formed, in addition to the main product, *p*-hydroxyazobenzene, the ortho compound to the extent of one per cent. of the weight of the aniline used.<sup>4</sup> Further, exceptions are also known in the naphthalene series; for example, the formation of *o*- and *p*-nitrobenzeneazo-2- $\alpha$ -naphthol in addition to the 4-azo derivative<sup>5</sup>,

<sup>1</sup> Limpricht: Ann. Chem. (Liebig), **263**, 236. See also Grandmougin and Freimann: Ber. d. chem. Ges., **40**, 3453.

<sup>2</sup> Ann. Chem. (Liebig), **263**, 236.

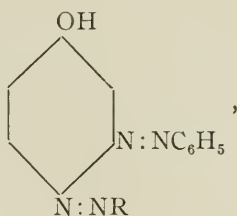
<sup>3</sup> Michel and Grandmougin: Ber. d. chem. Ges., **26**, 2353.

<sup>4</sup> Bamberger: *Ibid.*, **33**, 3188.

<sup>5</sup> Bamberger and Meimberg: *Ibid.*, **28**, 1889. Bamberger: *Ibid.*, **28**, 848.

and, according to a recent patent,<sup>1</sup> in the combination of diazo solutions (in the patent, *m*-hydroxy-*p*-diazobenzene-sulphonic acid) with  $\alpha$ -naphthol in extremely concentrated solutions of caustic alkali the azo group enters the ortho position.

It has not been possible, hitherto, to introduce more than two azo groups into the molecule of a monacid phenol or two azo residues into the ortho positions to the hydroxyl group. The work of Grandmougin and Freimann shows that with the introduction of two azo groups the limit of combination of phenol with diazonium salts is not yet attained and also that it is possible to introduce an azo group into both ortho positions to the hydroxyl group in a monacid phenol. Our work with the diacid phenol, resorcin, and the work of Perkin with the triacid phenol, phloroglucinol, shows that trisazo compounds, in which two of the azo groups are ortho and the other para to one of the hydroxyl groups, can be made with the greatest ease. Few attempts to make trisazo compounds are to be found in the literature. Besides the statement of Wallach and Fischer, mentioned above, and the trisazo compounds of phloroglucinol also noted, Jacobson and Hönigsberger<sup>2</sup> obtained, by combining *m*-hydroxyazobenzene with a diazonium salt, a phenoldisazo compound, to which they give the formula

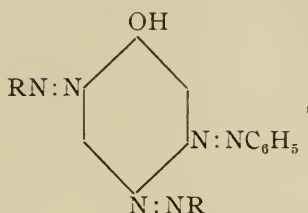


and they also consider the possibility of the formation of a trisazo product having the formula

<sup>1</sup> D. R. P. 14,443 (J. R. Geigy & Co.) Pat. Schriftensammlung der Chem. Z., No. 592 (1908).

<sup>2</sup> Ber. d. chem. Ges., **36**, 4093.





but they seem to have made no attempts to prepare this substance. If this trisazo compound can be made, there seems to be no reason why it would not be possible to introduce still another azo group into it in the position ortho to the hydroxyl group and thus make a tetrazo compound.

In the year 1904 Vignon<sup>1</sup> attempted to prepare the simplest trisazo compound, phenol-2,4,6-trisazobenzene, both by the action of three molecules of benzenediazonium chloride on one molecule of phenol and also by the action of one and two molecules of the diazonium chloride on hydroxyazobenzene and on phenoldisazobenzene in caustic alkaline solution. Curiously enough, he did not succeed in going beyond the disazo stage and he therefore designates the phenoldisazobenzene as the limit of combination of phenol with diazonium salts. In the year 1907, however, Toniolo made the observation that when two molecules of benzenediazonium chloride acted on an alkaline solution of one molecule of phenol, there was formed, in addition to the well-known 2,4-phenoldisazobenzene, a new compound in small amount. This compound had a much higher melting point than the disazo product and differed from it also in chemical properties and hence it was thought to be the phenol-2,4,6-trisazobenzene<sup>2</sup> which Vignon had failed to get. The investigation was then taken up by Grandmougin and Freimann, who showed that the product was really the above trisazo compound and that, contrary to the statement of Vignon, it could be obtained very readily and in considerable quantity when three molecules of the benzenediazonium chloride were allowed to act on one molecule of phenol in caustic alkaline solution.

<sup>1</sup> Compt. Rend., **138**, 1279.

<sup>2</sup> Grandmougin and Freimann: Ber. d. chem. Ges., **40**, 2662.

A great deal of work has been done of late years on the constitution of the hydroxyazo compounds, but it is impossible to review that work here. According to Auwers, who has devoted most time to this problem, these substances are all true azo compounds.<sup>1</sup> We shall therefore use the azo formulas in this article for all the azo compounds made by us.

#### EXPERIMENTAL.

##### *Resorcintrisazobenzene.*

As was stated above, it seemed likely that resorcintrisazobenzene would be formed if resorcin were treated with an excess of benzenediazonium chloride in caustic alkaline solution. The formation of such a compound was readily accomplished, the materials being used in the following proportions:

Resorcin (1 molecule), 11 grams; aniline (3 molecules), 27.9 grams; sodium nitrite (3 molecules), 20.7 grams; hydrochloric acid (7 molecules), 25.5 grams; sodium hydroxide (5 molecules), 20 grams.

The aniline, which was freshly distilled and pure, was dissolved in 500 cc. of dilute hydrochloric acid (sp. gr. 1.026), the solution cooled to 0° and stirred vigorously with a mechanical stirrer, while the nitrite, dissolved in 150 cc. of distilled water, was slowly added. The mixture was then stirred for twenty minutes, the temperature being kept at 0° to 5°. At the end of this time a trace of nitrous acid was still present, as shown by the reaction with starch-iodide paper.

The resorcin, dissolved in 100 cc. of distilled water, was added to the solution of the diazonium salt, the mixture stirred for ten minutes, and then poured slowly and with constant stirring into a large vessel containing the caustic soda dissolved in two liters of water and cooled down to about 0° with ice, a rise in temperature being prevented by the addition of ice from time to time.

The solution turned dark brown at once and a voluminous precipitate gradually formed. This mixture was then stirred for two days without further addition of ice and the dark brown

<sup>1</sup> Ann. Chem. (Liebig), 360, 11.

precipitate filtered off and thoroughly washed with water. The filtrate contained a small amount of resorcindisazobenzene, which was thrown down as a yellowish-brown precipitate on adding an excess of acid. The dark brown product was removed from the filter, treated with dilute hydrochloric acid, washed thoroughly with water, filtered off and dried. It was then repeatedly crystallized from a mixture of chloroform and alcohol, from benzene and again from chloroform until the melting point was constant. The product thus obtained consisted of brown cigar-shaped microscopic needles, which melted sharply at  $254^{\circ}$  (uncor.<sup>1</sup>).

Analyses of this product, dried in the water oven at about  $100^{\circ}$  to constant weight, gave the following results:

I. 0.5990 gram substance gave 1.4955 grams  $\text{CO}_2$  and 0.2366 gram  $\text{H}_2\text{O}$ .

0.1350 gram substance gave 24.55 cc. N ( $743.6 \text{ mm.}^2$  and  $21^{\circ} \text{ C.}$ ).<sup>3</sup>

II. 0.2157 gram substance gave 0.5391 gram  $\text{CO}_2$  and 0.0868 gram  $\text{H}_2\text{O}$ .

0.4266 gram substance gave 74.3 cc. N ( $754 \text{ mm.}$  and  $15^{\circ} \text{ C.}$ ).

	Calculated for $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_6$ . <sup>4</sup>	I.	Found.	II.
C	68.21	68.08		68.16
H	4.30	4.42		4.51
N	19.91	20.08 <sup>5</sup>		20.08

From these analyses there can be no doubt that the substance is resorcin\text{C}\_6\text{H}(\text{OH})\_2(\text{N}\_2\text{C}\_6\text{H}\_5)\_3.

It is soluble in benzene, toluene and xylene, in chloroform, ethyl acetate and glacial acetic acid, but only very slightly soluble in ether and in alcohol. It dissolves in an alcoholic

<sup>1</sup> The melting points given in this paper were taken with a thermometer compared with one standardized by the Physikalisch-Technische Reichsanstalt.

<sup>2</sup> The barometer used in all our determinations had a brass scale.

<sup>3</sup> This analysis was made for us by Mr. E. H. Nichols.

<sup>4</sup> International atomic weights for 1910 are used in all calculations in this paper.

<sup>5</sup> In calculating the percentage of nitrogen from the volume we used 1.2507 grams as the value for the weight of a liter of nitrogen, under standard conditions, given by Guye in the J. Chim. Phys., **5**, 218 (1907), and based on the results of Rayleigh, Ramsay and Gray. Professor F. W. Clarke, of the U. S. Geological Survey, has recalculated the value of the weight of a normal liter of nitrogen ( $0^{\circ} \text{ C.}$  and  $760 \text{ mm.}$  at sea level and  $45^{\circ}$  latitude) as 1.25066 grams, which is essentially that of Guye.

solution of the caustic alkalies with a reddish-brown color and in concentrated sulphuric acid it gives a deep bluish-violet solution.

The crystals from chloroform and alcohol were examined by Professor A. C. Gill, of the Mineralogical Department of Cornell University, who reports as follows: "The substance crystallizes in monoclinic or triclinic needles with strong pleochroism and an extinction angle of  $25^{\circ}$  to  $30^{\circ}$  as a maximum. The color of the small needles is light yellow to deep brownish-yellow in transmitted light, becoming so dark as to seem almost black when the stage of the microscope is turned."

*Diacetyl Derivative of Resorcintrisazobenzene.*—For the preparation of this compound, 1.3 grams of the pure resorcintrisazobenzene were boiled for thirty minutes with an equal weight of anhydrous sodium acetate and 15 grams of pure acetic anhydride in a flask provided with a return condenser. When cold, the mixture was poured into a saturated salt solution. The resulting oil soon solidified to a yellow crystalline mass, which was washed thoroughly with water and dried. It was then recrystallized from alcohol and from a mixture of alcohol and ethyl acetate until the melting point became constant. The compound thus obtained consisted of a mass of very fine golden yellow needles, which melted sharply at  $201^{\circ}$  (uncor.). Slow crystallization from ethyl acetate or from ether gave red pyramidal crystals which melted at  $203^{\circ}$  (uncor.). These red crystals are converted into the golden yellow needles on dissolving them in alcohol and quickly cooling the saturated solution. When the yellow needles are suspended in ether they are rapidly converted into the red pyramidal crystals, this change taking place more rapidly when the ether is boiled.

Analyses of the golden yellow needles gave the following results:

I. 0.1054 gram substance gave 0.2561 gram  $\text{CO}_2$  and 0.0440 gram  $\text{H}_2\text{O}$ .

II. 0.1376 gram substance gave 0.3344 gram  $\text{CO}_2$  and 0.0577 gram  $\text{H}_2\text{O}$ .

0.1982 gram substance gave 30.2 cc. N (735 mm. and  $23^{\circ}$ ).



	Calculated for $C_{28}H_{22}O_4N_6$ .	I.	Found. II.
C	66.38	66.27	66.28
H	4.38	4.68	4.53
N	16.61	...	16.45

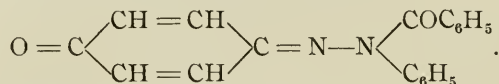
The compound is therefore the diacetyl derivative of resorcintrisazobenzene,  $C_6H(OCOCH_3)_2(N_2C_6H_5)_3$ . Professor Gill examined both the yellow and the red modifications of the diacetyl-resorcintrisazobenzene and found that the former crystallized in "yellow, very slightly pleochroic needles, with parallel or nearly parallel extinction, optically biaxial, positive, with the plane of the optical axes across the needles, and an optical angle of about  $70^\circ$ . They are probably monoclinic. The needles are about 0.01 mm. by 1 or 1.5 mm. in size."

In the case of the latter modification he states: "the brilliant red crystals show much variation in habitus, from tabular to stout columnar, to pyramidal. The tabular crystals are six-sided, and at first sight look as if monoclinic with the clinopinacoid as the principal face, the other boundaries being in the position of base, orthopinacoid and prism. They show oblique extinction, but also an obtuse bisectrix obliquely inclined to the large face, hence the crystallization is doubtless triclinic. Pleochroism is very marked, from clear yellow to deep red, and the double refraction is above 0.05."

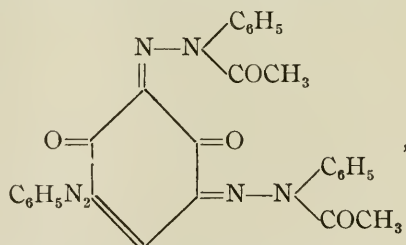
In order to determine which of the two forms of the diacetyl derivative is the more stable, the golden yellow needles were dissolved in absolute alcohol and the solution concentrated until it was saturated. A few of the red pyramidal crystals were then added and the solution allowed to cool very slowly. The resulting crystals consisted entirely of the red pyramidal form. This experiment was repeated, with acetic acid and then benzene as solvents, and only the red pyramidal crystals were obtained. Further work showed that the golden yellow needles are obtained only under special conditions, *viz.*, by quick cooling of a saturated solution or by precipitation with some solvent in which the compound is but slightly soluble. The red pyramidal crystals are therefore the stable form. The yellow needles do not contain any solvent of crystallization, such as alcohol or water, as was determined by

heating them in a Victor Meyer air bath to  $110^{\circ}$  for one hour. The loss in weight was only 0.12 per cent. The analyses of the compound also showed that it contained no solvent. Later the red pyramidal crystals were also analyzed and found to contain no solvent.<sup>1</sup>

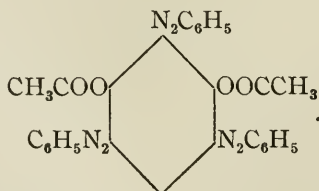
This conduct of the diacetylresorcintrisazobenzene is very similar to that of the quinonebenzoylphenylhydrazone made from quinone and benzoylphenylhydrazine:



McPherson<sup>2</sup> describes two crystal forms of this substance and Willstätter and Veraguth<sup>3</sup> add that it is dimorphous, forming light yellow prisms, which go over into reddish-yellow rhombohedra (almost cubical crystals) on covering them with ether or on heating them to about  $100^{\circ}$ , and slowly even on standing. This similarity in conduct might be used as an argument in favor of the quinonephenylhydrazone formula for the diacetylresorcintrisazobenzene,



instead of the one which would naturally be given to the substance:

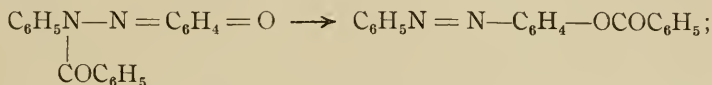


<sup>1</sup> See page 19.

<sup>2</sup> *THIS JOURNAL*, **22**, 364 (1899).

<sup>3</sup> *Ber. d. chem. Ges.*, **40**, 1434 (1907).

Now Willstätter and Veraguth<sup>1</sup> have shown that quinone-benzoylphenylhydrazone is readily transformed into benzoyl-hydroxyazobenzene by simply shaking the dry ethereal solution with pulverized caustic potash, the benzoyl group migrating from the nitrogen to the oxygen atom according to the scheme,



and we thought that if our diacetyl derivative were a quinone-phenylhydrazone it might act in a similar manner. On shaking it in solution in anhydrous ether with dry powdered caustic potash, however, even at 0°, the color of the solution changed from yellow to red and the solid alkali turned black. After five minutes the ether was removed and evaporated, the residue treated with dilute hydrochloric acid, and the resulting reddish-brown powder washed with water and dried. When crystallized from ethyl acetate it melted at 254° (uncor.), showing that the diacetyl derivative was saponified by this process, yielding the free trisazo compound.

It is impossible, therefore, to say whether the two forms of diacetylresorcintrisazobenzene represent stereoisomeric quinonephenylhydrazones or are simply two crystal modifications of the same substance. Possibly the isomerism may be similar to that suggested by Hantzsch and Robertson<sup>2</sup> to explain the yellow and red forms of the salts and hydrates of the hydroxyazo compound. They obtained the silver salt of hydroxyazobenzene almost always in a red modification, which was, however, so unstable that it changed into the yellow form even under the solution.

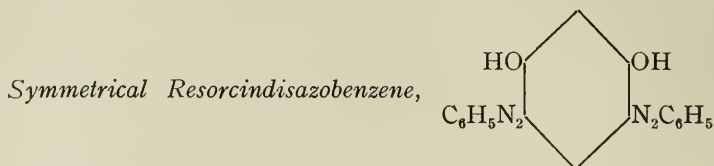
*Preparation of Resorcintrisazobenzene from the Symmetrical and the Unsymmetrical Resorcindisazobenzene.*

In order to determine the positions of the azo groups in the molecule of resorcintrisazobenzene, this compound was made from both the symmetrical and unsymmetrical resor-

<sup>1</sup> Ber. d. chem. Ges., **40**, 1434 (1907).

<sup>2</sup> *Ibid.*, **43**, 106 (1910).

cindisazobenzenes and the products compared with each other and with that made from three molecules of the diazonium salt and one of resorcin.<sup>1</sup> The two resorcindisazobenzenes were prepared according to the directions of Kostanecki.<sup>2</sup>



—In the preparation of this product the materials were used in the following proportions:

Resorcin (1 mol.), 22.0 grams; aniline (2 mols.), 37.2 grams; hydrochloric acid (5 mols.), 36.5 grams; sodium nitrite (2 mols.), 27.6 grams; sodium hydroxide (4 mols.), 32.0 grams.

The pure aniline was dissolved in 500 cc. of dilute hydrochloric acid (sp. gr. 1.0345) and the solution cooled with ice and stirred vigorously with a mechanical stirrer, while the nitrite, dissolved in 100 cc. of distilled water, was slowly added. After twenty minutes a slight excess of nitrous acid was shown to be present by means of starch-iodide paper. The resorcin, dissolved in 500 cc. of distilled water and cooled to 0°, was then added, the mixture stirred for ten minutes, and then poured slowly and with constant stirring into the caustic alkali dissolved in two liters of ice water. The solution turned deep red and a small amount of a dark precipitate separated. This mixture was stirred for twenty-four hours and allowed to warm up to room temperature gradually. The precipitate was then filtered off and the filtrate acidified. The voluminous yellowish-brown precipitate was washed with water till free from salts and then dried. After crystallization from chloroform and alcohol it melted sharply at 217° (uncor.) and corresponded in every respect with the description of the symmetrical resorcindisazobenzene given in the literature. It is soluble in chloroform, benzene, toluene, xylene, ethyl acetate and glacial acetic acid, slightly soluble

<sup>1</sup> See page 11.

<sup>2</sup> Ber. d. chem. Ges., **21**, 3117.



in alcohol, while it is almost insoluble in ether. Aqueous caustic alkalis dissolve it very readily and it is also taken up by concentrated sulphuric acid, forming a rose-colored solution.

*Diacetyl Derivative of Symmetrical Resorcindisazobenzene.*— This product was made in the same manner as the diacetyl-resorcintrisazobenzene. It was crystallized from alcohol and then from ethyl acetate until the melting point became constant. The light yellow needles thus obtained melted sharply at  $183^{\circ}$  (uncor.) and gave the following result on analysis:

0.1736 gram substance gave 0.4179 gram  $\text{CO}_2$  and 0.0721 gram  $\text{H}_2\text{O}$ .

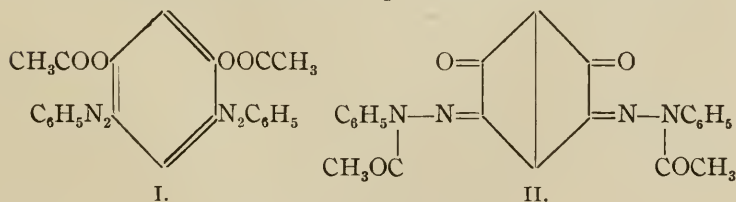
	Calculated for $\text{C}_{22}\text{H}_{18}\text{O}_4\text{N}_4$ .	Found.
C	65.65	65.65
H	4.50	4.65

The compound was therefore the diacetyl derivative of the symmetrical resorcindisazobenzene,



It is soluble in ethyl acetate, benzene, toluene, acetic acid, ether, alcohol and acetone. The crystals from ethyl acetate were examined by Professor Gill, who reports as follows: "The four-sided, needle-shaped crystals show only very slight pleochroism. They have a yellow color and an extinction angle of  $0^{\circ}$  to  $15^{\circ}$ . The double refraction is medium strong, plane of the optical axes across the direction of elongation and the optical character is positive. The system is probably monoclinic, the prisms being terminated by a clinodome which makes an angle of about  $25^{\circ}$  with the base. The base, however, is not developed and the angle was measured on a microscope stage and is only approximately correct."

Two structural formulas are possible for this substance:



Diacetylresorcindisazobenzene.

According as it is regarded as a true azo compound (I) or as

a quinone phenylhydrazone derivative (II). In order to determine which of these formulas is correct, the substance was treated with phenylhydrazine in alcoholic solution and also in acetic acid. In all cases the diacetyl product was saponified with the formation of the resorcindisazobenzene.

*Resorcintrisazobenzene from the Symmetrical Resorcindisazobenzene.*—In the preparation of the trisazo compound from the symmetrical resorcindisazobenzene the materials were used in the following proportions:

Symmetrical resorcindisazobenzene (1 mol.), 31.8 grams; sodium hydroxide (5 mols.), 20.0 grams; aniline (1 mol.), 9.3 grams; sodium nitrite (1 mol.), 6.9 grams; hydrochloric acid (3 mols.), 11.0 grams.

The disazo compound was placed in a large cylinder and the caustic soda dissolved in two liters of water poured over it, the mixture being stirred until complete solution took place, and then it was cooled by adding ice. In the meantime the aniline was dissolved in one liter of hydrochloric acid (sp. gr. 1.005) and converted into the diazonium salt in the usual way. This solution was then added slowly and with vigorous stirring to the ice-cold solution of the disazo compound in caustic soda. The deep red solution immediately turned dark brown and a heavy precipitate was formed. The mixture was stirred for twenty-four hours and allowed to warm up to room temperature gradually. The dark brown precipitate was then filtered off, washed with water, suspended in dilute hydrochloric acid, again filtered, washed and dried. After several crystallizations from a mixture of chloroform and alcohol and from benzene it melted sharply at  $254^{\circ}$  (uncor.) and had all the other properties characteristic of the trisazo compound already described. After drying in the water oven to constant weight it was analyzed:

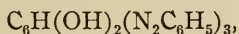
I. 0.2259 gram substance gave 0.5644 gram  $\text{CO}_2$  and 0.0885 gram  $\text{H}_2\text{O}$ .

II. 0.2241 gram substance gave 0.5604 gram  $\text{CO}_2$  and 0.0851 gram  $\text{H}_2\text{O}$ .

0.3081 gram substance gave 56.3 cc. N (737 mm. and  $23^{\circ}$ ).

	Calculated for $C_{24}H_{18}O_2N_6$ .	I.	Found. II.
C	68.21	68.14	68.20
H	4.30	4.39	4.25
N	19.91	...	19.78

The substance is therefore resorcintrisazobenzene,



and is identical with the product made by the action of three molecules of the diazonium salt on an alkaline solution of resorcin.

*Diacetyl Derivative of Resorcintrisazobenzene Made from the Symmetrical Disazo Compound.*—This product was made by the method already described. The two modifications, yellow needles melting at  $201^\circ$  and red pyramidal crystals melting at  $203^\circ$ , were obtained and shown to correspond in all respects to the diacetyl derivative made from the resorcintrisazobenzene obtained from resorcin by combining it with three molecules of the diazonium salt.

Analyses of the yellow needles (I) and of the red pyramidal crystals (II) show that these two forms have the same chemical composition:

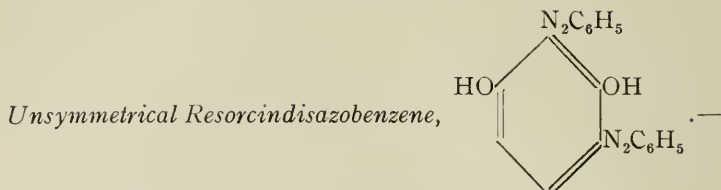
I. 0.17405 gram substance gave 0.4231 gram  $CO_2$  and 0.0698 gram  $H_2O$ .

II. 0.3854 gram substance gave 0.9386 gram  $CO_2$  and 0.1523 gram  $H_2O$ .

0.2746 gram substance gave 41.6 cc. N (743 mm. and  $21^\circ$ ).

	Calculated for $C_{28}H_{22}O_4N_6$ .	I.	Found. II.
C	66.38	66.30	66.42
H	4.38	4.49	4.43
N	16.61	...	16.71

When this diacetyl derivative is treated with phenylhydrazine at room temperature and the mixture is allowed to stand, it gradually warms up and an exceedingly vigorous reaction takes place, accompanied by charring and the formation of tarry substances.



The materials were used in the following proportions:

Resorcin (1 mol.), 22.0 grams; aniline (2 mols.), 37.2 grams; sodium nitrite (2 mols.), 27.6 grams; hydrochloric acid (5 mols.), 36.5 grams; sodium acetate (4 mols.), 65.6 grams.

The solution of the diazonium salt was prepared in the usual way, using 500 cc. of hydrochloric acid (sp. gr. 1.0345). The mixture of the diazonium salt and resorcin was poured slowly and with constant stirring into the sodium acetate dissolved in two liters of ice water. After stirring for two days the red precipitate was washed thoroughly by decantation, filtered off and dried. Crystallized from a mixture of chloroform and alcohol, the compound melted at  $221^{\circ}$  (uncor.) and corresponded in all other respects to the unsymmetrical resorcindisazobenzene described in the literature.

An analysis gave the following result:

0.1992 gram substance gave 0.4963 gram  $\text{CO}_2$  and 0.0844 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{18}\text{H}_{14}\text{O}_2\text{N}_4$ .	Found.
C	67.90	67.94
H	4.43	4.75

Professor Gill describes the crystals as "reddish needles with parallel extinction, strong double refraction and weak pleochroism. Absorption rather strong but yellow in *thin* layers made by rubbing with the finger nail."

*Diacetyl Derivative of Unsymmetrical Resorcindisazobenzene.*—This substance was prepared in the usual way. It crystallized from alcohol in yellow needles which melted sharply at  $137^{\circ}$  (uncor.). An analysis resulted as follows:

0.2336 gram substance gave 0.5610 gram  $\text{CO}_2$  and 0.0973 gram  $\text{H}_2\text{O}$ .

	Calculated for $C_{22}H_{18}O_4N_4$ .	Found.
C	65.65	65.50
H	4.50	4.66

According to Professor Gill, the "masses of extremely fine capillary crystals show parallel, or nearly parallel, extinction and slight pleochroism, the greater absorption being across the elongation of the needles." This diacetyl compound also reacts with phenylhydrazine in glacial acetic acid solution but no definite product could be isolated from the tarry residue obtained.

*Resorcintrisazobenzene from the Unsymmetrical Resorcindisazobenzene.*—The materials were used in the following proportions:

Unsymmetrical resorcindisazobenzene (1 mol.), 31.8 grams; sodium hydroxide (5 mols.), 20.0 grams; aniline (1 mol), 9.3 grams; sodium nitrite (1 mol.), 6.9 grams; hydrochloric acid (3 mol.), 11.0 grams.

The disazo compound was placed in a large glass cylinder with the alkali dissolved in four liters of water, and complete solution effected by passing in steam. The solution of the diazonium salt was then prepared by the method already given and added slowly and with constant stirring to the ice-cold alkaline solution of the disazo compound. The solution turned darker immediately and a heavy precipitate separated. This mixture was stirred for two days without further addition of ice. The precipitate was filtered off, washed thoroughly with water, suspended in dilute hydrochloric acid, washed, filtered and dried. On recrystallization from chloroform and alcohol and from benzene until the melting point became constant, the product was found to be identical with the trisazo compound prepared by the two methods already described.

A much purer product was obtained by dissolving the disazo compound in an alcoholic solution of caustic soda and then adding an aqueous solution of the diazonium salt. The aqueous solution of benzenediazonium chloride, prepared from 1.55 grams of aniline, 1.15 grams of sodium nitrite,



and 160 cc. of hydrochloric acid (sp. gr. 1.005), was added slowly and with constant stirring to an ice-cold solution of 5 grams of caustic soda and 5.3 grams of the disazo compound in two liters of absolute alcohol. The mixture was constantly stirred for 24 hours and allowed to warm up to room temperature gradually. Most of the trisazo compound remained in solution, but on acidifying fine reddish-brown needles were precipitated. Crystallization from benzene gave small, light brown, cigar-shaped needles, which melted sharply at  $254^{\circ}$  (uncor.). Analyses of the two products gave the following results:

I. 0.23765 gram substance gave 0.5935 gram  $\text{CO}_2$  and 0.0946 gram  $\text{H}_2\text{O}$ .

0.22005 gram substance gave 39.4 cc. N (742 mm. and  $21^{\circ}$ ).

II. 0.1158 gram substance gave 20.4 cc. N (747.8 mm. and  $15^{\circ}.5$ ).

	Calculated for $\text{C}_{24}\text{H}_{18}\text{O}_2\text{N}_6$ .	I.	Found. II.
C	68.21	68.11	...
H	4.30	4.46	...
N	19.91	19.71	20.10

The product is hence resorcintrisazobenzene.

*Diacetyl Derivative of Resorcintrisazobenzene Made from the Unsymmetrical Resorcindisazobenzene.*—This product was made by the method already described and found to be absolutely identical with the two specimens of diacetylresorcintrisazobenzene already made. The yellow needles melting at  $201^{\circ}$  (uncor.) were analyzed:

0.15505 gram substance gave 0.3779 gram  $\text{CO}_2$  and 0.0608 gram  $\text{H}_2\text{O}$ .

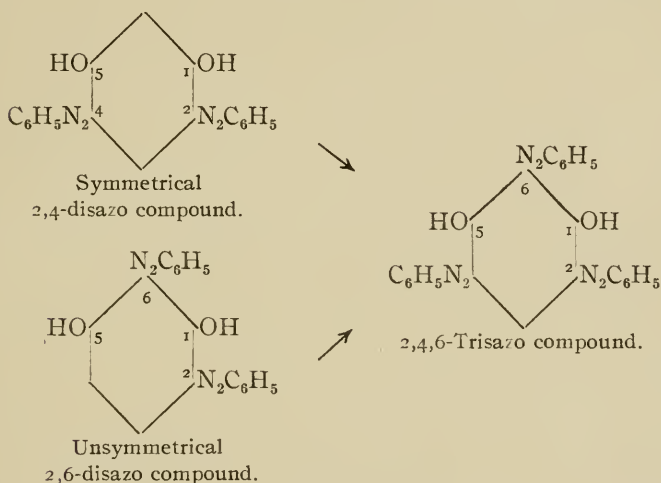
0.2095 gram substance gave 31.8 cc. N (739.5 mm. and  $22^{\circ}.5$ ).

	Calculated for $\text{C}_{28}\text{H}_{22}\text{O}_4\text{N}_6$ .	Found.
C	66.38	66.47
H	4.38	4.39
N	16.61	16.53

The product is hence diacetylresorcintrisazobenzene. It

crystallizes in the yellow and red modifications, which may be converted into each other by the methods already given.

Since it has been shown that the same resorcintrisazobenzene results from the combination of benzenediazonium chloride with the symmetrical and the unsymmetrical resorcindisazobenzenes, it follows that the azo groups must occupy the positions 2, 4 and 6. This is shown in the following scheme:



*The So-called  $\beta$ -Resorcindisazobenzene of Wallach and Fischer.*

The study of Wallach's so-called  $\beta$ -resorcindisazobenzene was next taken up. This compound was prepared by Wallach by combining one molecule of benzenediazonium chloride with resorcinazobenzene dissolved in four molecules of caustic potash. Two disazo compounds are formed here according to Wallach, one soluble and the other insoluble in aqueous alkalis. The first Wallach designates as the  $\alpha$ - and the second as the  $\beta$ -resorcindisazobenzene. The  $\alpha$  product yields a diacetyl derivative melting at 183° and is therefore the symmetrical 2,4-disazo compound, but the  $\beta$  product gives no well-crystallized acetyl derivative and its melting point is very difficult to determine accurately on account of its dark color. Important criteria for the absolute purity of the

$\beta$  compound are therefore lacking. Wallach gives the melting point at  $220^{\circ}$  and states that it was earlier<sup>1</sup> given at "about  $225^{\circ}$ ." He also states that the  $\beta$  compound dissolves in concentrated sulphuric acid with a pure indigo-blue color and in an alcoholic solution of caustic potash with a brownish-red color. The results of two determinations of carbon and hydrogen and one of nitrogen are given and these agree fairly well with the percentages of carbon, hydrogen and nitrogen calculated for the disazo formula,  $(C_6H_5N_2)_2C_6H_2(OH)_2$ , though the percentage of nitrogen found is nearly intermediate between that required for the disazo and the trisazo compounds.

In repeating the work of Wallach and Fischer, we first made resorcinazobenzene according to the directions of Kostanecki.<sup>2</sup> This was then converted into the so-called  $\beta$ -resorcin-disazobenzene according to the directions of Wallach and Fischer, using the materials in the following proportions:

Resorcinazobenzene (1 mol.), 21.4 grams; caustic potash (4 mols.), 22.4 grams; aniline (1 mol.), 9.3 grams; sodium nitrite (1 mol.), 6.9 grams; hydrochloric acid (3 mols.), 10.9 grams.

On running the solution of the diazonium salt into the alkaline solution of the monazo compound, a dark brown precipitate slowly separated. The mixture was stirred for twenty-four hours and allowed to warm up to room temperature gradually. The finely divided precipitate was filtered off, suspended in dilute hydrochloric acid, washed with water, filtered and dried.

This crude product was crystallized from a mixture of chloroform and alcohol. Brownish microscopic needles were thus obtained, which corresponded to Wallach's description, as they melted at  $221^{\circ}$  (uncor.), were insoluble in aqueous alkalis, dissolved in concentrated sulphuric acid with a blue color, and formed a brownish-red solution in alcoholic caustic potash. When repeatedly crystallized from benzene and then from chloroform the melting point of the product rose to  $228^{\circ}.5$  (uncor.). Several attempts were made to con-

<sup>1</sup> Ber. d. chem. Ges., **15**, 22.

<sup>2</sup> *Ibid.*, **21**, 3119.

vert this substance into an acetyl derivative, but without success. Nothing but tarry products were obtained. This is again in accord with Wallach's statements.

From the fact that this product was insoluble in aqueous alkalies, soluble in concentrated sulphuric acid with a blue color and in alkaline caustic potash with a brownish-red color, and from the method of preparation it was suspected that it was a trisazo compound. The product having the highest melting point,  $228^{\circ}.5$ , was then analyzed:

I. 0.0621 gram substance gave 11.25 cc N (733 mm. and  $21^{\circ}.5$ ).

II. 0.10325 gram substance gave 19.25 cc. N (730 mm. and  $25^{\circ}$ ).

N	Calculated for:		Found.	
	Resorcin- disazobenzene.	Resorcin- trisazobenzene.	I.	II.
	17.62	19.91	19.66	19.78

These analyses show that the product is resorcin*trisazo*-benzene and not the *disazo*benzene, as Wallach states. It differs, however, from the trisazo compound in its melting point and it was first thought that it might be a stereoisomer of this substance. Several attempts were therefore made to convert it into the trisazo compound melting at  $254^{\circ}$  by heating it with such high boiling solvents as xylene, nitrobenzene, etc., but no change took place. We then attempted to convert the trisazo compound melting at  $254^{\circ}$  into Wallach's  $\beta$  compound by dissolving it in alcoholic caustic potash, diluting with water and precipitating the compound with carbon dioxide. The product was dried in the air and recrystallized from chloroform. It melted at  $254^{\circ}$ , showing that it was unchanged by this treatment. Suspecting that the so-called  $\beta$  product was contaminated with a small amount of the symmetrical resorcin*disazo*benzene, which is soluble in aqueous solutions of the caustic alkalies, we made up a new lot of the  $\beta$  compound according to Wallach's directions and subjected the crude product to the following treatment: The material was suspended in two liters of a ten per cent. solution of caustic soda and the mixture treated with steam until it was near the boiling point and then filtered. The residue re-

maining on the filter was subjected to this treatment five or six times, with fresh sodium hydroxide solution each time, until it imparted but little color to the alkali solution. It was then suspended in dilute hydrochloric acid, washed with water, filtered and dried. The alkaline filtrates, when acidified, gave a voluminous precipitate of the symmetrical resorcin-disazobenzene melting at  $217^{\circ}$  (uncor.). The material insoluble in dilute caustic soda solution, when crystallized from a mixture of chloroform and alcohol and from benzene, gave at once a product melting at  $254^{\circ}$  and identical with the resorcin-trisazobenzene already described. It was then converted into the diacetyl derivative by the method given above and this was found to exist in the two modifications, yellow needles melting at  $201^{\circ}$  (uncor.) and red pyramidal crystals melting at  $203^{\circ}$  (uncor.), which could be converted into each other at will.

From these results it is evident that Wallach's so-called  $\beta$ -resorcindisazobenzene is an impure form of the resorcin-2,4,6-trisazobenzene.

*Resorcin-2,4,6-trisazo-p-toluene.*

This substance was prepared by the method already detailed in the preparation of resorcintrisazobenzene, substituting 32.1 grams of pure *p*-toluidine (3 mols.) for the 27.9 grams of aniline. The reddish-brown precipitate was filtered off after two days, thoroughly washed with water, suspended in dilute hydrochloric acid, again washed with water, filtered and dried. When repeatedly crystallized from a mixture of chloroform and alcohol and then from benzene until the melting point was constant, the product came out in the form of small reddish-brown needles which melted sharply at  $259^{\circ}$  (uncor.).

This compound is soluble in chloroform, benzene and toluene, slightly so in ethyl acetate and acetic acid, while it is practically insoluble in alcohol. It dissolves in alcoholic caustic potash with a reddish-brown color and in concentrated sulphuric acid, forming a reddish-violet solution.



Analyses showed that the compound is the resorcintrisazo-*p*-toluene,  $C_6H(OH)_2(N_2C_7H_7)_3$ .

0.24275 gram substance gave 40.4 cc. N ( $24^\circ$  and 737 mm.).

0.29925 gram substance gave 0.7651 gram  $CO_2$  and 0.1375 gram  $H_2O$ .

	Calculated for $C_6H(OH)_2(N_2C_7H_7)_3$ .	Found.
C	69.79	69.73
H	5.21	5.15
N	18.11	17.91

*Diacetyl Derivative of Resorcin-2,4,6-trisazo-p-toluene.*—This compound, made from the above product in the usual manner, crystallized from ethyl acetate and alcohol in yellow needles melting at  $218^\circ$  (uncor.). Analyses showed that it is the diacetyl derivative:

0.1885 gram substance gave 27.1 cc. N ( $20^\circ$  and 724 mm.).

0.19095 gram substance gave 0.4747 gram  $CO_2$  and 0.0865 gram  $H_2O$ .

	Calculated for $C_6H(OCOCH_3)_2(N_2C_7H_7)_3$ .	Found.
C	67.85	67.80
H	5.15	5.08
N	15.33	15.51

In its solubility and physical properties this substance resembles the diacetylresorcintrisazobenzene very closely. It may also be obtained in two modifications, yellow needles and red prismatic crystals, which may be converted into each other by the methods given under diacetylresorcintrisazobenzene. The conversion of the yellow needles into the red crystals does not seem to take place so readily, however, as the ethereal solution must be boiled for some time before the transformation is complete.

*Symmetrical Resorcindisazo-p-toluene.*

Resorcindisazo-*p*-toluene was made by Wallach and Fischer<sup>1</sup> by combining resorcinazo-*p*-toluene with the diazonium salt obtained from *p*-toluidine in caustic potash solution. They obtained an  $\alpha$  and a  $\beta$  compound, the latter in very considerable quantity. The  $\alpha$  product, which is soluble in caustic alkalies,

<sup>1</sup> Ber. d. chem. Ges., 15, 2824.

crystallizes in yellow felted needles, difficultly soluble in alcohol and cold chloroform, easily soluble in boiling chloroform, and melting at  $255^{\circ}$ – $256^{\circ}$ . Their  $\beta$  compound, insoluble in caustic alkalies, forms microscopic blackish-brown crystals, which, previous to crystallization from hot chloroform, dissolve in concentrated sulphuric acid with a red color and afterwards with a blue coloration. Melting point,  $202^{\circ}$ – $203^{\circ}$ . Analyses of both products are given and the percentages of carbon, hydrogen and nitrogen found, agree well with those required for the formula  $(C_7H_7N_2)_2C_6H_2(OH)_2$ . We made the symmetrical product by combining two molecules of *p*-toluenediazonium chloride and one of resorcin in sodium hydroxide solution, using the materials in the following proportions:

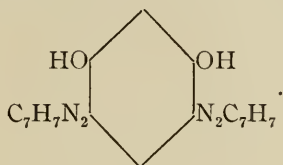
Resorcin (1 mol.), 11.0 grams; *p*-toluidine (2 mols.), 21.4 grams; sodium nitrite (2 mols.), 13.8 grams; hydrochloric acid (5 mols.), 18.25 grams; sodium hydroxide (4 mols.), 16.0 grams. The method given under the symmetrical resorcindisazobenzene was followed. The solution turned dark immediately on the addition of the diazonium salt and a dark brown precipitate formed. The mixture was stirred for two days without further addition of ice and then the dark brown precipitate, which was identical with Wallach's so-called  $\beta$ -resorcindisazo-*p*-toluene, was filtered off and laid aside for further study. On acidifying the filtrate a light brown precipitate was obtained, which was washed with water and dried. This was crystallized from chloroform and alcohol and gave reddish-brown needles melting at  $254^{\circ}$  (uncor.). It is soluble in chloroform, benzene, toluene, acetic acid, ethyl acetate, but only slightly soluble in alcohol and acetone. It dissolves in aqueous caustic alkalies with a reddish color and in concentrated sulphuric acid with a rose color. This compound is resorcindisazo-*p*-toluene, as shown by the following analyses:

0.1193 gram substance gave 18 cc. N ( $24^{\circ}$  and 735.5 mm.).

0.19775 gram substance gave 0.50095 gram  $CO_2$  and 0.09445 gram  $H_2O$ .

	Calculated for $C_6H_2(OH)_2(N_2C_7H_7)_2$ .	Found.
C	69.33	69.09
H	5.24	5.35
N	16.19	16.20

It is identical with Wallach's  $\alpha$  compound and from the method of formation it must have the symmetrical structure,



*Diacetyl Derivative of Symmetrical Resorcindisazo-p-toluene.*—

This compound, prepared in the usual way, crystallized from a mixture of ethyl acetate and alcohol in light lemon-yellow needles, which melted at  $198^{\circ}.5$  (uncor.) and gave the following result on analysis:

0.0797 gram substance gave 9.9 cc. N ( $22^{\circ}$  and 722 mm).

	Calculated for $C_6H_2(OCOCH_3)_2(N_2C_7H_7)_2$ .	Found.
N	13.03	13.23

Wallach's so-called  $\beta$ -resorcindisazo-*p*-toluene, which was obtained in the preparation of the symmetrical resorcindisazo-*p*-toluene, was next studied. Profiting by our experience in the investigation of the so-called  $\beta$ -resorcindisazobenzene of Wallach,<sup>1</sup> we placed the  $\beta$ -resorcindisazo-*p*-toluene in a large glass cylinder with two liters of a ten per cent. solution of caustic soda and passed steam into the mixture until it was near the boiling point. The hot solution was filtered and the process repeated until the residue imparted only a faint color to the alkali. It was then suspended in dilute hydrochloric acid, washed with water, filtered off and dried. On acidifying the filtrates from the above extractions the symmetrical resorcindisazo-*p*-toluene, melting at  $254^{\circ}$  (uncor.), was obtained.

Crystallization from chloroform and alcohol of the dried residue insoluble in the alkaline solution gave at once a product melting at  $259^{\circ}$  (uncor.), crystallizing in reddish-brown needles and corresponding in all other properties with the resorcintrisazo-*p*-toluene already described.<sup>2</sup> It gave a

<sup>1</sup> See page 23.

<sup>2</sup> See page 26.

diacetyl derivative crystallizing from ethyl acetate in yellow needles, melting at  $218^{\circ}$  and identical in all other properties with the diacetylresorcintrisazo-*p*-toluene already described. An analysis also proved this identity.

0.14845 gram substance gave 21.5 cc. N ( $25^{\circ}$  and 729 mm.).

	Calculated for $C_6H(OCOCH_3)_2(N_2C_7H_7)_3$ .	Found.
N	15.33	15.33

It seems highly probable from these results that Wallach's so-called  $\beta$ -resorcindisazo-*p*-toluene is in reality an impure resorcintrisazo-*p*-toluene from which he had not completely removed all of the disazo compound by his method of purification. The fact that this compound dissolves in concentrated sulphuric acid with a red color and, after purification by crystallization from hot chloroform, with a blue color indicates the same thing, since we have shown that the disazo product dissolves in sulphuric acid with a red color while the trisazo compound forms a reddish-violet solution in the same solvent.

*Unsymmetrical Resorcindisazo-p-toluene.*

As this compound had not been made we prepared it, using the materials in the following proportions:

Resorcin (1 mol.), 11 grams; *p*-toluidine (2 mols.), 21.4 grams; sodium nitrite (2 mols.), 13.8 grams; hydrochloric acid (5 mols.), 18.25 grams; sodium acetate (4 mols), 32.8 grams.

The *p*-toluidine was diazotized in the usual way and the resorcin added, the total amount of solvent being the same as in the preparation of the symmetrical resorcindisazo-*p*-toluene. The mixture was then poured slowly and with constant stirring into the sodium acetate dissolved in two liters of ice water. At first the combination takes place slowly and the reaction must be allowed to proceed at least two days. At the end of this time a beautiful salmon-colored precipitate had formed and this was washed thoroughly with water, filtered off and dried. When recrystallized from chloroform and alcohol it gave reddish-colored needles, melting at  $230^{\circ}.5$  (uncor.).

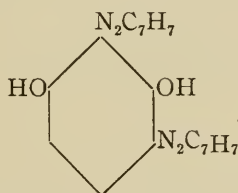
The compound is soluble in most of the organic solvents, but only slightly soluble in the aqueous caustic alkalis. On analysis it gave the following results:

0.17685 gram substance gave 26.2 cc. N ( $23^{\circ}$  and 740.5 mm.).

0.1418 gram substance gave 0.3613 gram  $\text{CO}_2$  and 0.0671 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}_2(\text{OH})_2(\text{N}_2\text{C}_7\text{H}_7)_2$ .	Found.
C	69.33	69.49
H	5.24	5.30
N	16.19	16.12

The product is therefore resorcindisazo-*p*-toluene and from its method of formation it must have the unsymmetrical structure:



*Diacetyl Derivative of the Unsymmetrical Resorcindisazo-*p*-toluene.*

This substance was made from the above compound in the usual way. Crystallized from ethyl alcohol and ethyl acetate it gave orange-yellow needles melting at  $150^{\circ}$  (uncor.). Analyses show that it is a diacetyl derivative:

0.1079 gram substance gave 12.9 cc. N ( $19^{\circ}$  and 733 mm.).

0.13135 gram substance gave 0.3214 gram  $\text{CO}_2$  and 0.0614 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}_2(\text{OCOCH}_3)_2(\text{N}_2\text{C}_7\text{H}_7)_2$ .	Found.
C	66.94	66.74
H	5.15	5.23
N	13.03	13.14

*Resorcin-2,4,6-trisazo-o-toluene.*

In the preparation of this substance the same proportions of materials and the same method were used as in the case of



the para compound,<sup>1</sup> ortho- being simply substituted for the paratoluidine. After two days the heavy brown precipitate was filtered off, suspended in dilute hydrochloric acid, washed with water, filtered and dried. Crystallization from chloroform and from benzene gave prismatic, reddish-brown crystals which melted at  $226^{\circ}$  (uncor.). The compound is soluble in chloroform, benzene, toluene, xylene and aniline, very slightly soluble in alcohol. In alcoholic caustic alkali it dissolves with a reddish-brown color and in concentrated sulphuric acid with a reddish-violet color.

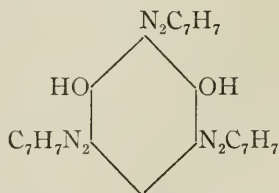
Analyses gave the following results:

0.16385 gram substance gave 27.3 cc. N ( $24^{\circ}$ .5 and 742 mm.).

0.18225 gram substance gave 0.4663 gram  $\text{CO}_2$  and 0.0859 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}(\text{OH})_2(\text{N}_2\text{C}_7\text{H}_7)_3$ .	Found.
C	69.79	69.77
H	5.21	5.28
N	18.11	18.03

The compound is therefore resorcintrisazo-*o*-toluene and it is quite likely that the azo groups occupy the positions 2, 4 and 6 in the molecule:



Professor Gill reports as follows regarding the crystals: "The extremely minute lens-shaped crystals have very strong pleochroism, absorption across the length of the crystals being complete, while that lengthwise is a fairly light reddish-yellow. No definite idea of the crystal system could be formed, except that they are not regular."

*Diacetyl Derivative of Resorcin-2,4,6-trisazo-o-toluene.*—This substance crystallize from ethyl acetate and alcohol in red-

<sup>1</sup> See page 26.

dish-brown needles melting at  $176^{\circ}$  (uncor.). It is a diacetyl derivative, as shown by the following analyses:

0.0744 gram substance gave 10.4 cc. N ( $22^{\circ}$  and 742 mm.).

0.11395 gram substance gave 0.2839 gram  $\text{CO}_2$  and 0.0521 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}(\text{OCOCH}_3)_2(\text{N}_2\text{C}_7\text{H}_7)_3$ .	Found.
C	67.85	67.95
H	5.15	5.13
N	15.33	15.32

The crystals were examined by Professor Gill, who reports as follows: "The thinner needles show light yellow color, the thicker ones reddish-brown. Pleochroism is weak. The extinction angle varies from  $0^{\circ}$  to  $15^{\circ}$ , depending on the position of the needles. Those with high extinction angles show so strong dispersion that the angle cannot be accurately determined. They are certainly monoclinic or triclinic, probably the former."

*Symmetrical Resorcindisazo-o-toluene.*

Wallach and Fisher made this compound but they give no analyses of the product. We made it, using the materials in the following proportions:

Resorcin (1 mol.), 11 grams; *o*-toluidine (2 mols.), 21.4 grams; sodium nitrite (2 mols.), 13.8 grams; hydrochloric acid (5 mols.), 18.25 grams; sodium hydroxide (4 mols.), 16.00 grams. The method given under the symmetrical resorcindisazo-*p*-toluene was followed. At the end of thirty-six hours the dark brown precipitate, which is identical with Wallach's so-called  $\beta$ -resorcindisazo-*o*-toluene, was filtered off and put aside. The filtrate, when acidified, gave a light red precipitate, which was washed with water, dried and crystallized from chloroform and alcohol. Brown needles and dumbbell-shaped aggregates which melted at  $197^{\circ}$  (uncor.) were obtained. Wallach<sup>1</sup> gives the melting point as  $194^{\circ}$ – $195^{\circ}$ . Analyses show that it is the disazo product:

0.0816 gram substance gave 12.3 cc. N ( $24^{\circ}$  and 742 mm.).

0.0847 gram substance gave 0.21495 gram  $\text{CO}_2$  and 0.0404 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}_2(\text{OH})_2(\text{N}_2\text{C}_7\text{H}_7)_2$ .	Found.
C	69.33	69.21
H	5.24	5.24
N	16.19	16.36

*Diacetyl Derivative of Resorcindisazo-o-toluene.*—This product crystallized from ethyl acetate and alcohol in yellow needles melting at  $178^\circ$  (uncor.), which gave the following results on analysis:

0.0969 gram substance gave 11.5 cc. N ( $23^\circ$  and 745 mm.).

0.1390 gram substance gave 0.3412 gram  $\text{CO}_2$  and 0.0681 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}_2(\text{OCOCH}_3)_2(\text{N}_2\text{C}_7\text{H}_7)_2$ .	Found.
C	66.94	66.94
H	5.15	5.49
N	13.03	12.99

Wallach's so-called  $\beta$ -resorcindisazo-*o*-toluene<sup>1</sup> was shown to be a mixture of disazo and trisazo compounds by extracting it several times with hot caustic soda solution by the method already given<sup>2</sup> and crystallizing the residue from chloroform and alcohol. The crystals thus obtained melted at  $222^\circ$  (uncor.) while the pure resorcintrisazo-*o*-toluene melts at  $226^\circ$  (uncor.). The amount of material was so small that further purification was not possible but it seems quite likely from this melting point and the work done on the other  $\beta$  compounds that this product is also a mixture of the disazo and trisazo compounds.

*Unsymmetrical Resorcindisazo-o-toluene.*

This compound was made in the same way as the para compound, simply substituting *o*-toluidine for the *p*-toluidine.<sup>3</sup> The mixture was allowed to react three days and then the salmon-red precipitate was filtered off, washed with water and dried. Crystallized from chloroform and alcohol it gave

<sup>1</sup> Ber. d. chem. Ges., **15**, 2825.

<sup>2</sup> See page 25.

<sup>3</sup> See page 30.

brilliant red needles melting at  $212^{\circ}$  (uncor.), soluble in chloroform, benzene, xylene and slightly in alcohol. They are soluble in alcoholic caustic alkalis with a red color and in concentrated sulphuric acid, forming a beautiful rose-colored solution. Analyses showed that it is the disazo product:

0.2363 gram substance gave 34.7 cc. N (745 mm. and  $22^{\circ}$ ).

0.1683 gram substance gave 0.4279 gram  $\text{CO}_2$  and 0.0799 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}_2(\text{OH})_2(\text{N}_2\text{C}_7\text{H}_7)_2$ .	Found.
C	69.33	69.34
H	5.24	5.32
N	16.19	16.15

Professor Gill states: "The crystals are somewhat flattened needles, with strong pleochroism and very high double refraction. The extinction angle reaches  $30^{\circ}$  as a maximum and is nearly zero as a minimum. The light transmitted vibrating in the direction of elongation is light yellowish in color, while that vibrating transversely is of a reddish hue. The crystals are either triclinic or monoclinic."

*Diacetyl Derivative of Unsymmetrical Resorcindisazo-o-toluene.*

This compound was prepared in the usual way and after crystallization from ethyl acetate and alcohol was obtained as orange-yellow needles melting at  $130^{\circ}$  (uncor.). Analyses resulted as follows:

0.14085 gram substance gave 17 cc. N ( $21^{\circ}$  and 732 mm.).

0.1214 gram substance gave 0.29865 gram  $\text{CO}_2$  and 0.0548 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}_2(\text{OCOCH}_3)_2(\text{N}_2\text{C}_7\text{H}_7)_2$ .	Found.
C	66.94	66.94
H	5.15	5.06
N	13.03	13.11

Professor Gill finds that "there are two kinds of crystals, one kind being apparently like those of the resorcintrisazo-o-toluene. The others are nonpleochroic or very slightly pleochroic, reddish-yellow needles with parallel extinction."

*Resorcin-2,4,6-trisazo- $\alpha$ -naphthalene.*

The following proportions of materials were used in the preparation of this substance:

Resorcin (1 mol.), 11 grams;  $\alpha$ -naphthylamine (3 mols.), 42.9 grams; sodium nitrite (3 mols.), 20.7 grams; hydrochloric acid (7 mols.), 25.5 grams; sodium hydroxide (5 mols.), 20 grams.

Owing to the fact that naphthalenediazonium chloride combines immediately with any unchanged  $\alpha$ -naphthylamine present, special precautions had to be taken in diazotizing the  $\alpha$ -naphthylamine. Very dilute solutions must be employed and the process carried out very rapidly. The 42.9 grams of  $\alpha$ -naphthylamine were suspended in four liters of water, the total amount of hydrochloric acid added and the mixture warmed until solution was effected. This solution was then cooled with ice to 0° and poured rapidly and with vigorous stirring into the sodium nitrite dissolved in one liter of ice water. If the process is carried out rapidly enough a perfectly clear solution of the diazonium salt results. To this, the resorcin, dissolved in 100 cc. of ice water, was added, the mixture stirred for 10 minutes and then poured slowly and with constant stirring into the alkali dissolved in two liters of ice water. The mixture was stirred for two days and gradually allowed to warm up to the temperature of the room. The heavy black precipitate was filtered off, suspended in dilute hydrochloric acid, washed thoroughly with water, filtered and dried. The yield of the trisazo compound was practically quantitative.

The dry product was then put into a large Soxhlet extractor and thoroughly extracted with absolute alcohol to remove substances soluble in this solvent. The residue left in the extractor, when crystallized from chloroform, gave small prisms having a cantharides-green luster. From benzene it comes out in clusters of prismatic needles melting at 253°. These were submitted to Professor Gill, who reports as follows: "Crystals absorb too strongly to transmit light even through the thinnest edges. On crushing, the very smallest fragments (under 0.001 mm.) show purplish and have an ex-



tion, thereby proving extremely high double refraction. The thin film made by crushing with the nail is clear purplish-red in transmitted light, not doubly refracting."

The compound is soluble in chloroform, benzene, toluene, xylene and aniline, very slightly soluble in ethyl acetate, acetone and glacial acetic acid, while it is insoluble in ether and alcohol. It dissolves in concentrated sulphuric acid with a reddish-violet color.

Analyses gave the following results:

I. 0.1268 gram substance gave 0.3511 gram  $\text{CO}_2$  and 0.0507 gram  $\text{H}_2\text{O}$ .

II. 0.1751 gram substance gave 0.4852 gram  $\text{CO}_2$  and 0.0681 gram  $\text{H}_2\text{O}$ .

0.0966 gram substance gave 13.15 cc. N ( $22^\circ$  and 730 mm.).

	Calculated for $\text{C}_6\text{H}(\text{OH})_2(\text{N}_2\text{C}_{10}\text{H}_7)_3$ .	I.	Found. II.
C	75.49	75.51	75.57
H	4.23	4.48	4.36
N	14.69	...	14.67

The compound is therefore resorcintrisazo- $\alpha$ -naphthalene.

*Diacetyl Derivative of Resorcin-2,4,6-trisazo- $\alpha$ -naphthalene.*—

On account of the slight solubility of the resorcintrisazo- $\alpha$ -naphthalene it was necessary to use a large amount of acetic anhydride in converting it into its diacetyl derivative. After boiling for several hours with a large excess of the anhydride, the material unacted on was filtered off and again boiled with fresh anhydride until it was all dissolved. The anhydride was then distilled off almost entirely, the residue poured into cold water, and the product crystallized from ethyl acetate and alcohol. Yellow prisms and cigar-shaped needles resulted, which melted sharply at  $228^\circ$  (uncor.). Analyses:

0.11665 gram substance gave 0.3121 gram  $\text{CO}_2$  and 0.04565 gram  $\text{H}_2\text{O}$ .

0.05965 gram substance gave 6.75 cc. N ( $19^\circ$  and 741 mm.).

	Calculated for $\text{C}_6\text{H}(\text{OCOCH}_3)_2(\text{N}_2\text{C}_{10}\text{H}_7)_3$ .	Found.
C	73.14	72.98
H	4.30	4.39
N	12.81	12.57

On boiling with ether these yellow needles go over into red tabular crystals, the transformation being similar to that observed in the case of the diacetyl derivative of resorcin-2,4,6-trisazobenzene.

The two forms are thus described by Professor Gill: "The very small capillary yellow crystals show no appreciable pleochroism and give extinction angles varying from  $0^{\circ}$  to several degrees. It behaves like the following modification, with which it may well be isomorphous."

"The extremely minute pleochroic blood-red to yellowish-red crystals are of stout tabular to columnar habitus and show parallel extinction in all positions. They are probably orthorhombic."

*Symmetrical Resorcindisazo- $\alpha$ -naphthalene.*

Many attempts were made to obtain this compound, but without success. When an alkaline solution of resorcin was treated with two molecules of  $\alpha$ -naphthalenediazonium chloride the resorcintrisazo- $\alpha$ -naphthalene resulted in every case and this compound was also obtained when resorcinazo- $\alpha$ -naphthalene in alkaline solution was treated with one molecule of the naphthalenediazonium salt.

*Unsymmetrical Resorcindisazo- $\alpha$ -naphthalene.*

The following proportions of materials were used in preparing this compound:

Resorcin (1 mol.), 2.75 grams;  $\alpha$ -naphthylamine (2 mols.), 7.15 grams; sodium nitrite (2 mols.), 3.45 grams; hydrochloric acid (5 mols.), 4.55 grams; sodium acetate (4 mols.), 8.20 grams.

The solution of the diazonium salt, prepared according to the directions already given, was added to the resorcin dissolved in 50 cc. of ice water. This mixture was then poured slowly and with constant stirring into the sodium acetate dissolved in one liter of ice water. The solution turns reddish at first, then brown, and finally a brown precipitate settles out. After stirring the mixture for two days the precipitate was filtered off, washed with water and dried. Repeated

crystallization from a mixture of chloroform and alcohol and from benzene until the melting point was constant gave very fine light brown needles, melting at  $242^{\circ}$  (uncor.), which dissolve in aqueous caustic soda with a reddish color. The following analyses show that it is the disazo compound:

0.11475 gram substance gave 0.31415 gram  $\text{CO}_2$  and 0.0484 gram  $\text{H}_2\text{O}$ .

0.08435 gram substance gave 10.3 cc. N ( $19^{\circ}$  and 726.5 mm).

	Calculated for $\text{C}_6\text{H}_2(\text{OH})_2(\text{N}_2\text{C}_{10}\text{H}_7)_2$	Found
C	74.61	74.66
H	4.34	4.72
N	13.40	13.29

*Diacetyl Derivative of Unsymmetrical Resorcindisazo- $\alpha$ -naphthalene.*—This product, made in the usual way from the disazo compound and crystallized from chloroform and alcohol, forms fine yellow needles melting at  $142^{\circ}$  (uncor.). Analyses made by Mr. J. K. Plummer gave the following results:

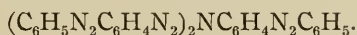
I. 0.1332 gram substance gave 14.3 cc. N at  $26^{\circ}$  C. Barometer 748 mm. at  $24^{\circ}.2$  C.

II. 0.1315 gram substance gave 13.95 cc. N at  $24^{\circ}$  C. Barometer 747 mm. at  $23^{\circ}$  C.

*See errata*  
*p. 596*

	Calculated for $\text{C}_6\text{H}_2(\text{OCOCH}_3)_2(\text{N}_2\text{C}_{10}\text{H}_7)_2$	I.	Found.	II.
N	11.16	11.61		11.59

*Bisazobenzene-p-diazoaminoazobenzene,*



This compound was obtained in an attempt to prepare a trisazo product by diazotizing *p*-aminoazobenzene and combining it with an alkaline solution of resorcin in the proportions of three molecules of the former to one of the latter. It is formed very readily on adding a cooled alcoholic solution of aminoazobenzene (3 mols.) and acetic acid (9 mols.) to a cold solution of sodium nitrite (2 mols.). Hence the compound is a condensation product of diazotized aminoazobenzene with aminoazobenzene. It crystallizes from 95 per cent. alcohol in yellow leaflets melting at  $184^{\circ}$  (uncor.).

It is insoluble in aqueous caustic alkalis, dissolves in concentrated sulphuric acid with a red color and in alcoholic caustic alkalis with a reddish-violet color. Analyses gave the following results:

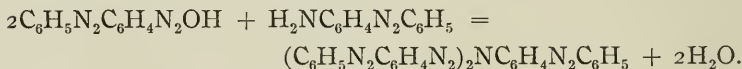
I. 0.1017 gram substance gave 0.2627 gram  $\text{CO}_2$  and 0.0419 gram  $\text{H}_2\text{O}$ .

II. 0.0717 gram substance gave 0.1850 gram  $\text{CO}_2$  and 0.0301 gram  $\text{H}_2\text{O}$ .

0.0493 gram substance gave 11.15 cc. N ( $22^\circ$  and 741 mm.).

	Calculated for ( $\text{C}_6\text{H}_5\text{N}_2\text{C}_6\text{H}_4\text{N}_2$ ) $_2\text{NC}_6\text{H}_4\text{N}_2\text{C}_6\text{H}_5$ .	I.	Found. II.
C	70.43	70.44	70.36
H	4.44	4.61	4.71
N	25.13	...	24.74

The product is therefore a bisdiaz amino compound formed according to the following equation:



Professor Gill thus describes the crystals: "The substance occurs in masses of overlapping plates which show distinct pleochroism—from brownish-yellow to pale yellow—a biaxial interference figure, medium double refraction and inclined extinction. The crystals are probably triclinic in form."

The more important facts brought out in this investigation may be briefly summarized as follows:

1. Resorcin-2,4,6-trisazobenzene has been prepared by the action of three molecules of benzenediazonium chloride on resorcin in caustic alkaline solution, as well as by the action of one molecule of the diazonium salt on the symmetrical and on the unsymmetrical resorcindisazobenzenes in caustic alkaline solution. This shows the position of the azo groups in the molecule to be 2, 4 and 6.

2. Wallach's so-called  $\beta$ -resorcindisazobenzene has been made and shown to be an impure product, containing resorcin-trisazobenzene mixed with some symmetrical resorcindisazo-

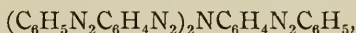
benzene. It is probable that Wallach's  $\beta$ -resorcindisazo-*o*- and *p*-toluenes are also impure trisazo compounds.

3. The diacetyl derivative of resorcin-2,4,6-trisazobenzene has been made and shown to exist in two modifications, one crystallizing from absolute alcohol in yellow needles and the other from ether in red pyramidal crystals, the latter being the more stable form.

4. Resorcin-2,4,6-trisazo-*o*- and *p*-toluenes and their diacetyl derivatives, and the unsymmetrical resorcindisazo-*o*- and *p*-toluenes and their diacetyl derivatives have been made.

5. Resorcin-2,4,6-trisazo- $\alpha$ -naphthalene has been prepared and converted into its diacetyl derivative, which also exists in two modifications, one crystallizing from alcohol in yellow needles, the other in red pyramidal crystals. The unsymmetrical resorcindisazo- $\alpha$ -naphthalene and its diacetyl derivative have also been made.

6. Bisazobenzene-*p*-diazoaminoazobenzene,



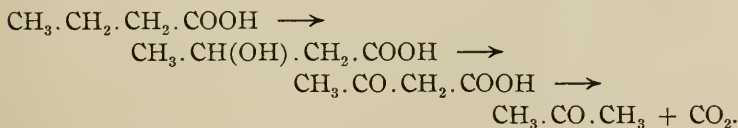
has been made and described.

CORNELL UNIVERSITY,  
ITHACA, N. Y.,  
March, 1910.

## A GENERAL REACTION FOR THE CONVERSION OF SATURATED FATTY ACIDS ( $\text{R}.\text{CH}_2.\text{CH}_2.\text{COOH}$ ) INTO KETONES ( $\text{R}.\text{CO}.\text{CH}_3$ ).

BY H. D. DAKIN.

It is a well established fact that in the diabetic organism butyric acid is oxidized to  $\beta$ -hydroxybutyric acid, and the latter substance is converted by the action of enzymes<sup>1</sup> present in the liver into acetacetic acid, which in part loses carbon dioxide with formation of acetone:



<sup>1</sup> Cp. Wakeman and Dakin: J. Biol. Chem., 6, 373.



There is good reason to believe that an essentially similar series of reactions takes place in the normal animal, but under physiological conditions the  $\beta$ -hydroxybutyric acid and acetacetic acid are quantitatively decomposed so that they are not found in normal urine.

From results recently obtained by the writer it appears probable that acetacetic acid is the primary product of oxidation of butyric acid in the animal body and that the acetacetic acid thus formed undergoes asymmetric reduction in the liver to *l*- $\beta$ -hydroxybutyric acid.

The type of oxidation represented by the conversion of butyric acid into  $\beta$ -hydroxybutyric and acetacetic acids, regarded from a purely chemical point of view, is a very remarkable one, and some writers have refused to accept excellent biochemical evidence of its occurrence on the ground that no purely chemical analogy for such a reaction was known.

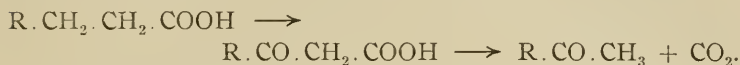
Three years ago the writer<sup>1</sup> showed that by a suitable choice of oxidizing agent it was possible to oxidize butyric acid outside the body in a way that bore a close resemblance to its mode of oxidation in the living organism. It was found that when neutralized with ammonia and digested at a low temperature (37°) with hydrogen peroxide it was converted in part into acetacetic acid and acetone. If the substances were gently boiled together, the yield of acetone was quite large. Under favorable conditions as much as fifty per cent. of the theoretical amount of acetone, calculated upon the amount of butyric acid actually oxidized, was obtained. Among other products of oxidation the following were detected: propionic aldehyde, acetic aldehyde, acetic and formic acids and carbon dioxide. No  $\beta$ -hydroxybutyric acid could be detected.

On further investigation it was found that the same type of reaction could be demonstrated to occur in the case of some higher fatty acids.<sup>2</sup> The object of the following paper is to record the results of further experiments which show that the reaction is a general one. In every case it has been

<sup>1</sup> J. Biol. Chem., **4**, 77.

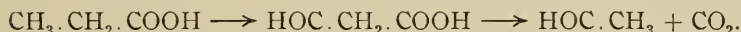
<sup>2</sup> *Ibid.*, **4**, 221.

possible to demonstrate the formation of a ketone by boiling a solution of the ammonium salt of a higher fatty acid with hydrogen peroxide and it is natural to infer that the ketone is derived from a  $\beta$ -ketonic acid, as is undoubtedly the case when butyric acid is oxidized with formation of acetone:



It was considered possible that fatty acid superoxides of the type described by Brodie<sup>1</sup> might be intermediary products in the process of oxidation. This appears unlikely, however, since butyryl superoxide, prepared by the action of barium peroxide upon an ethereal solution of butyric anhydride, failed to yield significant amounts of acetone when boiled with water or dilute alkali.

Propionic acid, when oxidized under the same conditions as those adopted in the case of butyric acid, yields acetaldehyde. It is possible, though perhaps unlikely, that this is also a case of oxidation of an acid in the  $\beta$  position, with formation of the half aldehyde of malonic acid as an intermediate step, followed by subsequent decomposition into acetaldehyde and carbon dioxide:



Acetic acid, on the other hand, yields glyoxylic acid and formaldehyde, together with much formic acid.<sup>2</sup>

Similar results were also obtained on oxidizing the phenyl derivatives of fatty acids; phenylacetic acid yields benzaldehyde, while phenylpropionic acid and phenylbutyric acid yield acetophenone and benzylmethylketone(?), respectively.

The results are collected in the following table, in which no cognizance is taken of products of oxidation other than ketones and aldehydes. In its present form the reaction under consideration is of no value for preparative purposes, since the yields are usually so small—averaging not more than 5–10 per cent.:

<sup>1</sup> J. Chem Soc., **1863**, 317.

<sup>2</sup> Cp. Hopkins: P. Roy. Soc., **67**, 21.

Acid oxidized.	Product.
Acetic acid.	Glyoxylic acid : formaldehyde (Hopkins).
Propionic acid.	Acetaldehyde.
<i>n</i> -Butyric acid.	Acetone
Isobutyric acid.	Acetone.
<i>n</i> -Valeric acid.	Ethylmethyl ketone.
Isovaleric acid.	Acetone.
<i>n</i> -Caproic acid.	Propylmethyl ketone.
Caprylic acid.	Amylmethyl ketone.
Nonylic acid.	Hexylmethyl ketone.
Capric acid.	Heptylmethyl ketone.
Lauric acid.	Nonylmethyl ketone.
Myristic acid.	Undecylmethyl ketone.
Palmitic acid.	Tridecylmethyl ketone.
Stearic acid.	Quindecylmethyl ketone.
Phenylacetic acid.	Benzaldehyde.
Phenylpropionic acid.	Acetophenone.
Phenylbutyric acid.	Benzylmethyl ketone(?)

## EXPERIMENTAL.

The methods employed in the experiments to be recorded were very simple and require but little description.<sup>1</sup> The oxidations in all cases were carried out by heating, to a point just short of active boiling, a mixture of the fatty acid, neutralized with a slight excess of ammonia or caustic soda and a large excess of dilute (3 per cent.) hydrogen peroxide. The materials are contained in large flasks connected with a reflux condenser, since foaming is apt to be very troublesome, particularly in the case of the higher fatty acids. The exact amount of hydrogen peroxide is of no great consequence, since under the most favorable conditions only a part of the fatty acid undergoes oxidation. Using 2 molecules of peroxide and one molecule of fatty acid, the proportion of fatty acid oxidized is less than ten per cent. in the case of the acids higher than caproic acid, but more than ten per cent. in the case of the lower fatty acids.<sup>2</sup>

In the case of the fatty acids up to and including lauric acid, the liquid containing the products of oxidation was

<sup>1</sup> Cp. papers in J. Biol. Chem., already referred to.

<sup>2</sup> Cp. J. Biol. Chem., 4, 229.

distilled. The distillate contains the ketone usually mixed with some aldehydes and also contains ammonia when that base was used for neutralizing the fatty acid prior to oxidation. The distillates from caprylic, nonylic, capric and lauric acids contain ketones which are very sparingly soluble in water and the oil drops are readily separated from the aqueous portion of the distillate and converted into a characteristic crystalline derivative. For purposes of identification, the *p*-nitrophenylhydrazones were found very useful.<sup>1</sup>

The distillate from the fatty acids lower than caprylic acid were treated as follows: A small quantity of Tollen's ammoniacal silver solution containing caustic soda was added and the mixtures allowed to stand for about an hour in order to oxidize any aldehyde present. They were next acidified strongly with phosphoric acid and redistilled. The ketones coming over in the first portion of the distillate were then identified by conversion into crystalline derivatives.

The ketones obtained from the oxidation of myristic, palmitic and stearic acids were isolated as follows: The alkaline mixture containing the products of oxidation was acidified with sulphuric acid and the precipitated fatty acids, ketone, etc., filtered off and washed. The precipitate was then dissolved in excess of alcoholic potash and evaporated to small bulk; the soapy residue was then dissolved in hot water and the solution extracted with ether. The ethereal solution, which is apt to contain traces of soap, is well washed with water and the ether distilled off. The residue is distilled from a small flask under reduced pressure. The distillate collected at about the temperature at which the ketone would be expected to distil is recrystallized from dilute alcohol and identified by melting point and by analysis:

A brief summary of the results upon which the identification of the products of oxidation is based is appended:

*Propionic Acid.*—The acetaldehyde was converted into the *p*-nitrophenylhydrazone, melting at 128°, <sup>2</sup> and was further identified by the usual reactions.

<sup>1</sup> Cp. J. Biol. Chem., 4, 235.

<sup>2</sup> Hyde: Ber. d. chem. Ges., 32, 1810.

*Butyric Acid.*—The acetone produced by the oxidation of butyric acid was identified by conversion into dibenzylidenacetone, melting at  $111^{\circ}.5$ – $112^{\circ}.5$  on treatment with benzaldehyde and caustic soda, and also into the *p*-nitrophenylhydrazone, melting at  $149^{\circ}$ .<sup>1</sup> (Analysis: C = 56.2, H = 5.9;  $C_9H_{11}O_2N_3$  requires C = 56.0, H = 5.7.)

*Isobutyric Acid.*—The methods of identification were the same as those employed in the case of *n*-butyric acid.

*n*-*Valeric Acid.*—The ethylmethyl ketone obtained on oxidation gave the *p*-nitrophenylhydrazone, melting at  $128^{\circ}$ , which crystallizes from alcohol in long yellow needles. (Analysis: C = 58.2, H = 6.5;  $C_{10}H_{13}O_2N_3$  requires C = 57.9, H = 6.3.)

*Isovaleric Acid.*—The acetone was identified as in the case of butyric acid.

*n*-*Caproic Acid.*—Propylmethyl ketone was obtained on oxidation and converted into the *p*-nitrophenylhydrazone, which crystallizes from alcohol in long golden prismatic needles, melting at  $117^{\circ}$ . This substance has not been previously described and was therefore prepared for purposes of comparison from a specimen of pure propylmethyl ketone of other origin. The two substances were identical in every respect. (Analysis: N = 18.8 per cent.;  $C_{11}H_{15}O_2N_3$  requires 19.0 per cent. N.)

*Caprylic Acid.*—The oily amylmethyl ketone from the oxidation of this acid was identified by conversion into the semicarbazone, melting at  $122^{\circ}$ – $123^{\circ}$ .<sup>2</sup>

*Nonylic Acid.*—The hexylmethyl ketone was identified by conversion into the *p*-nitrophenylhydrazone, which after repeated crystallization from alcohol was obtained in the form of aggregates of yellow prisms melting at  $92^{\circ}$ – $93^{\circ}$ . For purposes of comparison the same substance was prepared from hexylmethyl ketone of other origin.

*Capric Acid.*—Heptylmethyl ketone was identified by means of its semicarbazone, which, after recrystallization from alcohol, melted at  $118^{\circ}$ – $119^{\circ}$ . The substance was identical

<sup>1</sup> J. Biol. Chem., 4, 77.

<sup>2</sup> Cp. J. Biol. Chem., 4, 221.



with that previously prepared by Thoms and by Soden and Henle.

*Lauric Acid.*—The sparingly soluble volatile oily ketone was identified by conversion into the *p*-nitrophenylhydrazone and also the semicarbazone melting at  $122^{\circ}$ – $122^{\circ}.5$ . The nitrophenylhydrazone crystallizes from alcohol in yellow needles often arranged in rosette form, melting at  $90^{\circ}$ – $91^{\circ}$ . The product was identical with that obtained from methyl-nonyl ketone of other origin. (Analysis: C = 66.8, H = 8.8;  $C_{17}H_{27}O_2N_3$  requires C = 66.9, H = 8.8.)

*Myristic Acid.*—The products of oxidation of myristic acid were treated with potash and then extracted with ether in the manner referred to on p. 45. On distilling the ether residue from a small flask a small quantity of undecylmethyl ketone was obtained from the fraction boiling between  $245^{\circ}$ – $265^{\circ}$ . It was crystallized from a little cold dilute alcohol and melted at  $27^{\circ}$ – $28^{\circ}$ , agreeing with Krafft's<sup>1</sup> observations. (Analysis: C = 78.6, H = 13.3;  $C_{13}H_{26}O$  requires C = 78.8, H = 13.1.)

*Palmitic Acid.*—Tridecylmethyl ketone was obtained from the fraction boiling below  $200^{\circ}$  under 22 mm. pressure. It was recrystallized from alcohol and melted at  $39^{\circ}$ —the melting point given by Krafft.

*Stearic Acid.*—Quindecylmethyl ketone was obtained from the fraction boiling below  $210^{\circ}$  under 20 mm. pressure. It crystallized from alcohol in large glistening, irregularly formed plates, melting at  $48^{\circ}$ – $49^{\circ}$ . (Analysis: C = 79.9, H = 13.3;  $C_{17}H_{34}O$  requires C = 80.3, H = 13.4.)

*Phenylacetic Acid.*—This acid was oxidized in the way that had already proved serviceable in the case of phenylpropionic acid.<sup>2</sup> Benzaldehyde was readily identified by conversion into the phenylhydrazone, melting at  $156^{\circ}$ . Small amounts of aromatic hydroxy acids were formed at the same time.

*Phenylpropionic Acid.*—A description of the oxidation of

<sup>1</sup> Ber. d. chem. Ges., **12**, 1667; **15**, 1724.

<sup>2</sup> J. Biol. Chem., **4**, 428.

this acid has already been published.<sup>1</sup> Acetophenone was readily obtained and identified by conversion into the *p*-nitrophenylhydrazone melting at 184°–185°. Aromatic hydroxy acids were also formed.

*Phenylbutyric Acid.*—The oxidation of phenylbutyric acid was carried out as in the case of phenylpropionic acid. It was easy to demonstrate the formation of a volatile ketone with the odor of benzylmethyl ketone, but with the small amount of acid (3.0 grams) available for oxidation it was not found possible to obtain a sufficient amount of the ketone, free from contaminating aldehydes formed simultaneously, to obtain the nitrophenylhydrazone in the pure state. The ketone reacted in the iodoform and nitroprusside tests in the same manner as pure benzylacetone.

LABORATORY OF DR. C. A. HERTER,  
NEW YORK.

## THE CATALYTIC RACEMIZATION OF OPTICALLY ACTIVE HYDANTOIN DERIVATIVES AND OF RELATED SUBSTANCES AS THE RESULT OF TAUTOMERIC CHANGE.

BY H. D. DAKIN.

The optically active  $\alpha$ -amino acids of the general type  $R.CH.NH_2.COOH$  are readily converted by the action of potassium cyanate into the salts of the corresponding uramido

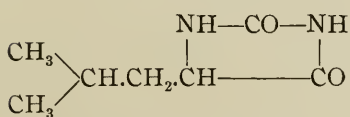
acids,  $R.CH \begin{matrix} \nearrow NH.CO.NH_2 \\ \searrow COOH \end{matrix}$ , and then by the action of boiling dilute mineral acids are transformed into the corre-

sponding hydantoins,  $R.CH \begin{matrix} \nearrow NH-CO \\ | \\ \searrow CO-NH \end{matrix}$ , through loss of a molecule of water. A study of a number of these derivatives of amino acids has recently been made since they appear to possess some biological significance. In the course of this investigation it was found convenient to ob-

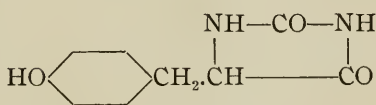
<sup>1</sup> J. Biol. Chem., 4, 419.

serve the optical activity of both the uramido acids and the hydantoins in alkaline solutions, since most of them are sparingly soluble in water but readily form soluble salts. It was found that under these conditions the optical rotation of the uramido acids was constant, whereas the rotation of the hydantoin derivatives steadily diminished until after the lapse of many hours the solution was optically inactive. On acidifying the solution which had originally contained the optically active hydantoin, the inactive hydantoin was recovered in every case, showing that the change that the substance had undergone was simply that of racemization. The inactive products thus obtained were in several instances compared with the hydantoins obtained synthetically from optically inactive amino acids.

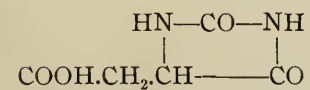
The following optically active hydantoins have in each case shown a rapid loss of optical activity when dissolved in normal caustic soda solution:



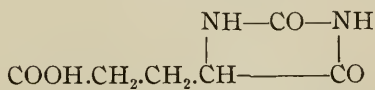
Isobutylhydantoin prepared  
from *l*-leucine.



*p*-Hydroxybenzylhydantoin prepared  
from *l*-tyrosine.



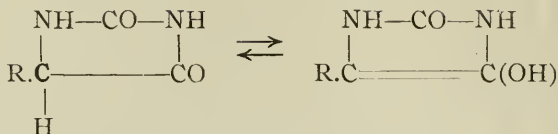
Hydantoinacetic acid prepared  
from *l*-aspartic acid.



Hydantoinpropionic acid prepared  
from *d*-glutamic acid.

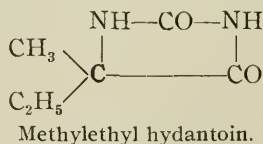
It was clearly of interest to try to elucidate the mechanism of this curious process of racemization. The fact that, in contrast with the optically active hydantoins, the active uramido acids show no trace of any such change in optical activity under like conditions indicated that the process of racemization was intimately connected with the presence of the CH—CO grouping. It was considered likely that the salts of the hydantoins might be derived from two tautomeric forms of hydantoin, only one of which contains an asym-

metric carbon atom. The two forms may be represented as follows:



Containing asymmetric carbon atom. No asymmetric carbon atom.

It is clear that such a type of tautomerism, if occurring in the hydantoin salts, would furnish a ready explanation of their racemization in the presence of alkali. Fortunately, it has been possible to make what appears to be a crucial test of this hypothesis. Owing to the kindness of Dr. Felix Ehrlich, a small quantity of *l*-methylethylaminoacetic acid (isovalin) was placed at my disposal and this was converted in the usual way, successively, into the corresponding uramido acid and hydantoin. The resulting methylethyl hydantoin was optically active but showed no sign of racemization in the presence of alkali. The reason of this is obviously to be sought in the absence of a labile hydrogen atom, without which the type of tautomeric change indicated



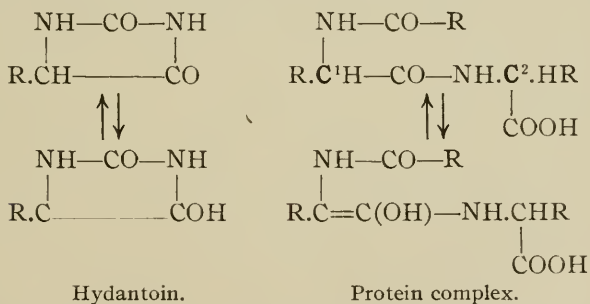
above cannot take place.

In the light of the above experiment, it can hardly be doubted that tautomeric change of the keto-enol type takes place in the salts of hydantoins containing the  $-\text{CH}-\text{CO}-$  grouping, and such an explanation adequately accounts for all the observed facts. I am unaware of the previous description of tautomerism of this type among the cyclic ureides.

The course of the racemization of the active hydantoins may be readily followed by means of the polarimeter. The reaction is apparently a monomolecular one, but the change has not yet been followed with great accuracy. The nature of the alkali exerts a profound influence upon the speed of

racemization. Thus, in an experiment in which hydantoin-acetic acid was dissolved in 0.25 N alkali so that 4 molecules of alkali were present to 1 molecule of hydantoin, 90 per cent. racemization was reached in 20 hours in the case of barium hydroxide, 33 hours with sodium hydroxide and 55 hours when ammonia was used. These differences may be due to the varying dissociation of the individual alkalies and salts. Provided sufficient time is allowed to elapse, complete racemization of 1 molecule of hydantoin may be effected by less than 1 molecule of alkali.

Since the molecular arrangement of the hydantoin ring bears a close resemblance to the groupings of amino acid radicals present in protein molecules, it was thought probable that proteins and their derivatives would also exhibit racemization phenomena when digested with dilute alkali. The groupings in the two cases may be compared as follows:



It was found that on dissolving egg albumin, gelatin, protamine, or Witte's peptone in normal caustic soda, a marked diminution in rotatory power was observed after the lapse of a few hours and it steadily continued for several days. Thus a solution of egg albumin in 0.5 N caustic soda<sup>1</sup> had an initial rotation of  $-1^{\circ}.40$  in a 200 mm. tube. After standing at room temperature for a week the value of  $\alpha$  had fallen to  $-0^{\circ}.82$ . Under similar conditions a solution of peptone in N sodium hydroxide<sup>2</sup> had an initial rotation of  $-9^{\circ}.44$ , which fell to  $-2^{\circ}.0$  after five days. In no case did the op-

<sup>1</sup> The solution contained 0.169 per cent. nitrogen.

<sup>2</sup> The solution contained 1.18 per cent. nitrogen.

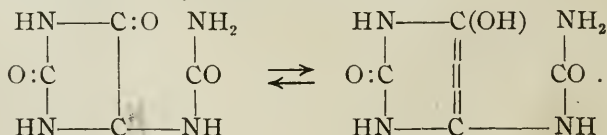


tical activity entirely disappear. This is in complete accord with what one would anticipate, since the hypothesis advanced would indicate that only those amino acid groupings which have undergone mutual condensation with elimination of water would be racemized. Free amino acid groupings,  $\text{—CHR.NH—COOH}$ , such as are undoubtedly present

in protein molecules, would be unaffected, since here, as in the case of the uramido acids, keto-enol tautomerism cannot occur. Thus for the two asymmetric carbon atoms present in the protein complex (see formula above), racemization would occur only in relation to the asymmetric group marked (1), and not in the case of that marked (2).

After my observations on the racemization of proteins had been made, I learned that Kossel and Weiss<sup>1</sup> had made similar experiments about a year previously. A careful study of the products of hydrolysis of "racemized proteins" would undoubtedly furnish valuable results, and such an investigation is, I believe, planned by Professor Kossel.

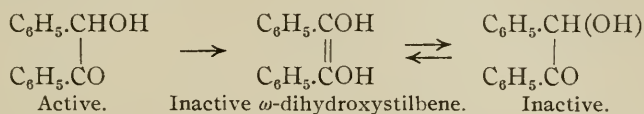
The conception of racemization due to keto-enol tautomeric change has recently been applied by Mendel and the writer to account for the optical inactivity of allantoin.<sup>2</sup> The customary formula for allantoin contains an asymmetric carbon atom, yet the substance, when isolated from natural sources, such as the urine of dogs fed with thymus, is constantly inactive and all attempts to resolve the inactive substance by chemical or biological methods have failed. Now allantoin may be regarded as the ureide of hydantoin and may be assumed to exhibit tautomerism of the same kind as is observed in the case of other hydantoin derivatives. The result of such tautomeric change would obviously lead to an optically inactive product, since one of the two tautomeric forms contains no asymmetric carbon atom:



<sup>1</sup> Z. physiol. Chem., **59**, 492.

<sup>2</sup> J. Biol. Chem., **5**, 153.

In conclusion, reference may be made to an interesting paper by Wren,<sup>1</sup> in which he shows that the racemization of *l*-benzoin and its methyl ether is probably to be referred to keto-enolic change:



The racemization of *d*- $\beta$ -methylhydrindone observed by Kipping,<sup>2</sup> and the conversion of *l*-menthone into *d*-menthone may also be due to tautomeric change of a similar kind.

#### EXPERIMENTAL.

*d*- $\alpha$ -Uramidoisobutylacetic Acid.—The laevorotatory leucine which served for the preparation of this acid was obtained by the hydrolysis of gelatin and was purified by conversion into the ethyl ester which was fractionated *in vacuo* and then hydrolyzed by boiling with water. The leucine was then repeatedly crystallized from water. It is unlikely, however, that the product was optically absolutely pure, since it is extremely difficult to obtain preparations of leucine entirely free from its isomers. The conversion into the uramido acid was readily effected by mixing leucine (5 grams) with potassium cyanate (5 grams) and adding 20 cc. of water. The mixture was then evaporated on the water bath almost to dryness. The residue was dissolved in a little hot water, filtered, and the crude uramido acid precipitated by the addition of hydrochloric acid. The yield of uramido acid amounts to about 70 per cent. of the theoretical amount. The substance was purified by repeated crystallization from boiling water and separates in the form of prismatic needles, melting at 205°–206°<sup>93</sup> with effervescence.

Analysis:

0.2130 gram substance gave 0.3705 gram CO<sub>2</sub> and 0.1590 gram H<sub>2</sub>O.

<sup>1</sup> J. Chem. Soc., **95**, 1593.

<sup>2</sup> P. Chem. Soc., **18**, 34. J. Chem. Soc., **95**, 167.

<sup>93</sup> Lippich (Ber. d. chem. Ges., **41**, 2963) obtained this substance by the action of urea upon leucine in the presence of baryta. The melting point is given as 189°. It is possible that Lippich's substance was partly racemized.

	Calculated for $C_7H_{14}O_3N_2$ .	Found.
C	48.28	47.91
H	8.04	8.29

The optical rotation was observed by dissolving the substance in normal caustic soda solution:

$$c = 3.15, l = 2.0, \alpha = +1^\circ.25, \text{ hence } [\alpha]_D^{20} = +1^\circ.9.$$

No change in the rotation was observed after the solution had stood for more than 48 hours.

*1-Isobutylhydantoin*.—On boiling *d*- $\alpha$ -uramidoisobutylacetic acid with ten per cent. hydrochloric acid (10 parts) for half an hour the substance was readily converted into the corresponding hydantoin, which crystallized out on cooling in transparent prismatic needles, melting at  $212^\circ$ . The substance is readily purified by recrystallization from boiling water.

Analysis:

0.1430 gram substance gave 0.2802 gram  $CO_2$  and 0.1003 gram  $H_2O$ .

	Calculated for $C_7H_{12}O_2N_2$ .	Found.
C	53.25	53.44
H	7.70	7.79

The optical rotation was observed in normal caustic soda solution.

$$c = 1.925, l = 2.20, \alpha = -2^\circ.83, \text{ hence } [\alpha]_D^{20} = -68^\circ.2.$$

After five hours the value for  $\alpha$  had fallen to  $-1^\circ.0$ , after 16 hours to  $-0^\circ.20$ , while after 30 hours the solution was optically inactive.

*i*- $\alpha$ -Uramidoisobutylacetic Acid.—This substance was obtained from synthetic optically inactive leucine by the same method as that employed in the case of the active substance. The inactive uramido acid appears to be slightly more soluble in water than the active isomer and crystallizes from water in small platelets, which frequently arrange themselves in such a fashion that to the unaided eye they have the appearance of needles. After repeated crystallization from water the substance melts at  $206^\circ$ – $208^\circ$ .

Analysis:

0.1481 gram substance gave 0.2610 gram CO<sub>2</sub> and 0.1032 gram H<sub>2</sub>O.

0.1851 gram substance gave 0.02968 gram nitrogen.

	Calculated for C <sub>7</sub> H <sub>14</sub> O <sub>3</sub> N <sub>2</sub> .	Found.
C	48.28	48.13
H	8.04	7.74
N	16.09	16.03

*i*-Isobutylhydantoin.—This substance was obtained by boiling the inactive uramido acid with ten parts of ten per cent. hydrochloric acid and also by acidifying the alkaline solutions of the active hydantoin after they had stood for several days at the ordinary temperature and had become entirely optically inactive. The products from the two different sources showed no difference in properties. The substance crystallizes from water, in which it is moderately soluble, in needles which, after repeated crystallization, melt at 211°–214°.

Analysis:

0.0964 gram substance gave 0.1904 gram CO<sub>2</sub> and 0.0709 gram H<sub>2</sub>O.

	Calculated for C <sub>7</sub> H <sub>12</sub> O <sub>3</sub> N <sub>2</sub> .	Found.
C	53.85	53.75
H	7.70	8.17

*l*-Parahydroxybenzylhydantoin.—This substance has already been described under the incorrect name of tyrosinehydantoin. It was detected by Blendermann<sup>1</sup> in the urine of rabbits which had received very large doses of tyrosine, but the writer has shown in a paper which will appear shortly in the *Journal of Biological Chemistry* that the substance was probably produced by the interaction of excreted tyrosine and urea as a result of the method of urine analysis adopted by Blendermann. The substance has also been obtained by Lippich.<sup>2</sup> The following was found to be the most advantageous method of preparation: Pure *l*-tyrosine obtained from the hydroly-

<sup>1</sup> Z. physiol. Chem., **6**, 234.

<sup>2</sup> Ber. d. chem. Ges., **41**, 2973.

sis of proteins<sup>1</sup> is suspended in 10 parts of actively boiling water and solid potassium cyanate is added rapidly in small portions until the tyrosine is completely dissolved. Dilute sulphuric acid (1 : 4) is then added until the solution is strongly acid and the liquid is then boiled under a reflux condenser for half an hour. On cooling, the hydantoin separates out in the form of aggregates of white needles. The yield is excellent. The melting point varies somewhat with the quantity of substance taken and with the speed of heating, but I have never found the variations to extend beyond the limits of 258°–263°. Using minute quantities of substance and heating moderately rapidly, the melting point is practically constant at 259°–262° (uncorr.). Blendermann, however, gives 275°–280° as the melting point, while Lippich records 242°–245° without commenting on the higher value of Blendermann.

Analysis:

0.1666 gram substance gave  $\text{NH}_3 = 0.02275$  gram N.

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2$ .	Found.
N	13.59	13.66

The rotation was observed in normal sodium hydroxide solution and showed a steadily diminishing normal value on standing.

$$\alpha = -5^\circ.35, l = 2.0, c = 1.866, \text{ hence } [\alpha]_D^{20} = -143^\circ.$$

After 2.5 hours the value of  $\alpha$  had fallen to about half and after 17 hours the solution was entirely inactive.

*i-Parahydroxybenzylhydantoin*.—The inactive substance we obtained from racemic tyrosine by the same method as that employed in the case of the active substance. It was also obtained by acidifying the alkaline solution of the active compound after complete loss of optical activity, and lastly it was also obtained by mixing equivalent quantities of the *d* and *l* compounds and recrystallizing from water. It was possible to carry out the last experiment only on a small

<sup>1</sup> The specimen used was obtained from the autolysis of kidney cell-juice. The specific rotation in 4 per cent. hydrochloric acid was  $-12^\circ.5$ .



scale, owing to the difficulty in obtaining the dextro compound. A small amount was obtained from certain animal experiments, to be described shortly in the *Journal of Biological Chemistry*. The inactive hydantoin melts at  $258^{\circ}$ – $260^{\circ}$  (uncorr.). When prepared from racemic tyrosine the product tended to crystallize in nodular aggregations of prisms, whereas the other preparations crystallized in the form of platelets.

Analysis:

0.1822 gram substance gave 0.3889 gram  $\text{CO}_2$  and 0.0818 gram  $\text{H}_2\text{O}$ .

0.1763 gram substance gave  $\text{NH}_3 = 0.02394$  gram N.

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_3\text{N}_2$ .	Found.
C	58.25	58.21
H	4.85	4.99
N	13.59	13.58

*l*-Hydantoinacetic Acid.—In order to obtain this substance *l*-aspartic acid (5.0 grams), potassium cyanate (6.0 grams) and water (25 cc.) were evaporated on the water bath. The residue was dissolved in excess of dilute (10 per cent.) hydrochloric acid and after boiling for 15 minutes the filtered solution was concentrated to about 25 cc. and allowed to crystallize in an ice chest. The *l*-hydantoinacetic acid, which is sparingly soluble, slowly crystallizes out and is purified from any contamination with potassium salts by recrystallization from water. The substance forms large, thick, highly refractive prisms, which begin to sinter at about  $212^{\circ}$  and melt at  $220^{\circ}$ – $225^{\circ}$ . The same substance has been obtained by Grimaux<sup>1</sup> by heating aspartic acid and urea and by Lippich by heating  $\alpha$ -uramidossuccinic acid with hydrochloric acid. These authors record slightly lower melting points, but this may be due to admixture with the racemic compound. The specific rotation was determined in normal caustic soda solution:

$$\alpha = -13^{\circ}.12, l = 2.2, c = 4.781, [\alpha]_D^{19} = -125^{\circ}.$$

After six hours the value of  $\alpha$  had fallen to about half the

<sup>1</sup> Bull. Soc. Chim., [2] 24, 337, and Compt. Rend., 81, 325 (1875).

original value, after eleven hours it was reduced to one-quarter, while at the end of thirty hours the solution was no longer optically active. The specific rotation varies with the concentration of both substance and alkali. The specific rotation of 0.988 per cent. solutions in 0.25 N caustic soda, ammonia and baryta were found to be  $-141^\circ$ ,  $-131^\circ$  and  $-131^\circ$ , respectively. As was mentioned in the introduction, these solutions underwent racemization at different rates. The baryta solution became inactive after about 42 hours, followed by the caustic soda solution in about 55 hours, while the ammonia solution required about 90 hours. The temperature varied from  $18^\circ$ – $20^\circ$  throughout the observations.

*i-Hydantoinacetic Acid.*—On acidifying and concentrating the solutions of the laevo compound in caustic soda after the optical activity had vanished, crystals of the inactive compound were readily obtained. The substance resembles the laevo compound closely, but melts at a slightly higher temperature,  $225^\circ$ – $228^\circ$ , first slightly sintering. The substance crystallizes in large, highly refractive prisms.

Analysis:

0.1688 gram substance gave 0.2382 gram  $\text{CO}_2$  and 0.0608 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_6\text{H}_6\text{O}_4\text{N}_2$	Found.
C	37.98	38.49
H	3.80	4.00

*l-Hydantoinpropionic Acid.*—The compound was obtained from *d*-glutamic acid (10.0 grams) and potassium cyanate (7.0 grams) by the same method as was employed for the *l*-hydantoinacetic acid. The substance is somewhat more soluble in water than its homologue and has a marked tendency to form supersaturated solutions. It crystallizes from water in large prismatic needles melting at  $179^\circ$ – $181^\circ$ .

Analysis:

0.3229 gram substance, dried at  $100^\circ$ , gave 0.4927 gram  $\text{CO}_2$  and 0.1386 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_7\text{H}_8\text{O}_5\text{N}_2$	Found.
C	41.86	41.61
H	4.65	4.77

*see errata*  
*p. 596*

The specific rotation in aqueous solution underwent no change on standing for 3 days at 20°.

$$\alpha = -3^{\circ}.05, c = 2.00, l = 2.2, \text{ hence } [\alpha]_D^{20} = -50^{\circ}.0.$$

The specific rotation in normal caustic soda was higher than in water and the value of  $\alpha$  steadily diminished on standing.

$$\alpha = -6^{\circ}.95, c = 4.00, l = 2.2, \text{ hence } [\alpha]_D^{23} = -79^{\circ}.$$

The rotation of a 2.26 per cent. solution in normal caustic soda fell to one half in 3.5 hours and the solution was entirely inactive after 18 hours.

*l-Hydantoinpropionic Acid*.—On acidifying the alkaline solutions of the active variety of this substance after optical activity had vanished, and concentrating, the inactive hydantoin was readily obtained. It crystallized in large, well-formed, transparent prisms which melt sharply at 167°–169°. In all respects save that of optical activity this substance closely resembles its laevorotatory isomer.

*d-Methylethylhydantoin*.—A small quantity of *l*-methylethylaminoacetic acid (*l*-isovalin) most kindly presented by Dr. Felix Ehrlich served for the preparation of this hydantoin. The amino acid, which had been obtained by the resolution of the inactive acid by Ehrlich's yeast method,<sup>1</sup> was converted into the sparingly soluble methylethyluramidoacetic acid by warming with potassium cyanate and precipitating with hydrochloric acid. The uramido acid, on account of the small amount available, was not recrystallized but was at once converted into the hydantoin by evaporation with 5 per cent. hydrochloric acid. The hydantoin was a sparingly soluble substance, crystallizing in transparent prisms, melting at 172°–173°.

Analysis:

0.1338 gram substance gave  $\text{NH}_3 = 0.0287$  gram N.

	Calculated for $\text{C}_5\text{H}_{10}\text{O}_2\text{N}_2$ .	Found.
N	21.54	21.45

<sup>1</sup> Biochem. Z., 8, 438.

The substance was dextrorotatory in normal caustic soda solution and the value of  $\alpha$  showed no change after standing for four days. The actual value for the specific rotation cannot be stated with accuracy, since there is no guarantee that the laevorotatory amino acid from which it was prepared was free from the inactive acid.<sup>1</sup> The rotation observed was as follows:

$$\alpha = +0^{\circ}.81, l = 2.0, c = 1.247, [\alpha]_D^{20} = +32^{\circ}(?).$$

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## THE FRIEDEL AND CRAFTS REACTION WITH CHLORIDES OF UNSATURATED ACIDS.

BY E. P. KOHLER, G. L. HERITAGE AND M. C. BURNLEY.

The following investigation was undertaken in connection with the preparation of an extensive series of  $\alpha,\beta$ -unsaturated ketones for the purpose of comparison by physical measurements. Many of these ketones are very easily obtained by the Schmidt-Claissen<sup>2</sup> condensation of an aldehyde with a saturated ketone; but with aliphatic aldehydes, and with aromatic aldehydes in which the carbonyl group is in an aliphatic side chain, the method generally gives aldols from which water is eliminated with difficulty, or else complex products not closely related to unsaturated ketones. We decided, therefore, to ascertain to what extent the Friedel and Crafts reaction can be used for preparing such ketones. The investigation led to the discovery of a number of facts of general interest in connection with the Friedel and Crafts reaction. These are published in this paper.

The literature on the subject under investigation is meager. The reaction was first applied to unsaturated chlorides by Stockhausen and Gattermann<sup>3</sup> in 1892. These investigators started with the chlorides of cinnamic and phenylpropionic acids, and obtained an excellent yield of the expected unsat-

<sup>1</sup> The methylethylaminoacetic acid employed possessed a specific rotation of  $-9^{\circ}.1$  in 5 per cent. aqueous solution.

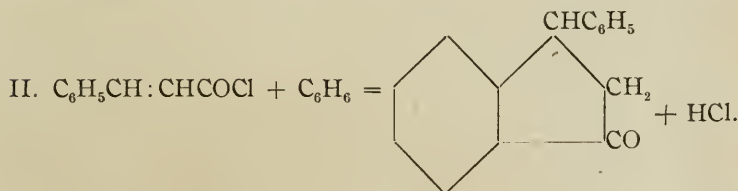
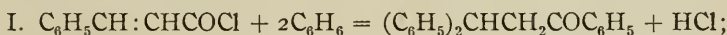
<sup>2</sup> Ber. d. chem. Ges., **13**, 2342.

<sup>3</sup> *Ibid.*, **25**, 3536.

urated ketone when they used anisol or phenetol, but could isolate no solid products when they used aromatic hydrocarbons. They attributed this result to the difference in the reactivity of phenol ethers and hydrocarbons.

Many years later Moureu<sup>1</sup> studied the reaction between the chloride of acrylic acid and benzene in the presence of aluminium chloride. He isolated a small quantity of a solid product that he assumed to be vinylphenyl ketone, but which was, in reality,  $\alpha$ -hydrindone. It was shown, a few years ago, that a satisfactory yield of unsaturated ketone can be obtained both with crotonyl chloride and benzene<sup>2</sup> and with cinnamyl chloride and mesitylene.<sup>3</sup>

We have found that the reaction between cinnamyl chloride and benzene takes place almost as readily as that between the same chloride and phenol ethers, but the product is a mixture of two saturated ketones—diphenylpropiophenone and phenylhydrindone:



A reaction between crotonyl chloride and benzene, similar to that represented by the first equation, was described in an earlier paper. It was there pointed out that such a result might be due either to the addition of hydrogen chloride to the unsaturated ketone first formed, and subsequent reaction with a second molecule of benzene, or to 1,4-addition of an organic aluminium compound to the same unsaturated ketone. We have not succeeded in getting any conclusive evidence in favor of either of these mechanisms.

The reaction expressed by the second equation represents a new indene synthesis which differs from that devised by

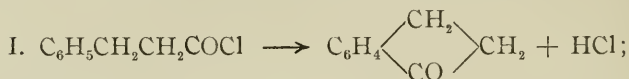
<sup>1</sup> Ann. Chim. Phys., [7] 2, 193.

<sup>2</sup> THIS JOURNAL, 42, 375.

<sup>3</sup> Ibid., 38, 510.



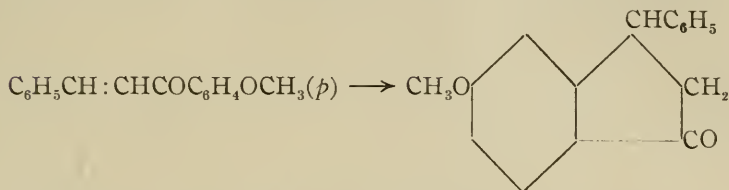
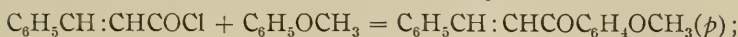
Kipping in that a benzene nucleus introduced by means of the Friedel and Crafts reaction, and not one already present in the acid chloride, forms the foundation of the bicyclic system. The difference is illustrated by the following equations, which represent the synthesis of  $\alpha$ -hydrindone:



The difference in the results obtained when cinnamyl chloride is condensed with benzene and with anisol may be due, in part, to the greater reactivity of phenol ethers, as assumed by Stockhausen and Gattermann; but this is certainly not the principal factor. With crotonyl chloride and benzene it is possible to conduct the reaction so as to get, at will, either saturated or unsaturated ketone. In concentrated solutions and at low temperatures the product is the unsaturated ketone, because, under these conditions, the aluminium chloride derivative of this ketone is so sparingly soluble that it separates quickly and thus escapes further reaction. In more dilute solutions and at a higher temperature the aluminium chloride derivative remains in solution long enough to react with a second molecule of benzene, and this process takes place so readily that when only one equivalent of benzene is used nearly half of the acid chloride is left unchanged. The determining factor in this case is, therefore, the solubility of the aluminium chloride derivative of the unsaturated ketone.

The reactions with cinnamyl chloride cannot be controlled like those with crotonyl chloride because the double compound between the acid chloride and aluminium chloride is so slightly soluble that it is necessary to use higher temperatures and more dilute solutions. Phenol ethers give unsaturated ketones, nevertheless, because the alkoxyl groups hinder or prevent the secondary reactions that lead to saturated compounds. Thus indene synthesis does not take place

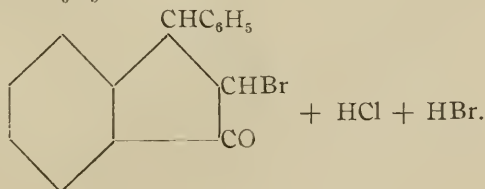
because this would necessitate closure of the second ring in the meta position with reference to alkoxy:



Our experiments show that the secondary reaction involving addition of a molecule of phenol ether to the unsaturated ketone first formed is likewise impossible—probably owing to the stability of the double compounds that alkoxy ketones, as well as phenol ethers, form with aluminium chloride. For similar reasons it is just as easy to get unsaturated ketones by using mesitylene as it is by using phenol ethers.

These results showed that the Friedel and Crafts reaction can be used in exceptional cases only for making  $\alpha,\beta$ -unsaturated ketones. As these substances are easily made by removing bromine from  $\alpha,\beta$ -dibrom ketones, we also made some experiments for the purpose of determining to what extent these can be made by condensing the chlorides of  $\alpha,\beta$ -dibrom acids with aromatic hydrocarbons.

Collet<sup>1</sup> added aluminium chloride to a solution of  $\alpha,\beta$ -dibromhydrocinnamyl chloride in benzene, and obtained a solid, melting at  $86^\circ$ , which he assumed to be benzalacetophenone dibromide. We obtained the same product, but found that Collet had misinterpreted the reaction. The substance contains but one atom of bromine. As it gives *o*-benzoylbenzoic acid on oxidation, it must be an indene derivative formed according to the equation:



<sup>1</sup> Compt. Rend., 125, 306.

Similar products were obtained when the same acid chloride was used with other aromatic compounds. The yield was poor in all cases because aluminium chloride attacks the acid chloride itself at the lowest temperature at which it is possible to carry out the reactions.

With chlorides of the corresponding dibrom aliphatic acids, however, the Friedel and Crafts reaction gives an excellent yield of dibrom ketones.

#### EXPERIMENTAL PART.

*Cinnamyl Chloride and Benzene.*—In the first experiments equimolecular quantities of chloride and hydrocarbon were dissolved in carbon bisulphide and treated with aluminium chloride, but we found that the product always contained a large quantity of unchanged chloride. This was the case, also, when the acid chloride was first transformed into the Perrier double compound with aluminium chloride and this treated with one molecule of benzene dissolved in carbon bisulphide. In all subsequent experiments the hydrocarbon was, therefore, used in excess. The reaction was studied under the following conditions:

1. In carbon bisulphide cooled in a freezing mixture ( $-20^{\circ}$ ). No perceptible reaction took place in the dark. In direct sunlight the aluminium chloride dissolved, then the Perrier double compound separated in small yellow crystals which redissolved, very slowly, with evolution of hydrochloric acid.

2. In carbon bisulphide at the ordinary temperature. The aluminium chloride dissolved with brisk evolution of hydrochloric acid and the reaction was complete after the addition of slightly more than one molecule of aluminium chloride.

3. The double compound between cinnamyl chloride and aluminium chloride was made in carbon bisulphide, the solvent removed by decantation and the crystalline solid covered with benzene. The reaction that started in the dark was completed in the sunlight.

The orange-colored liquids obtained in these reactions were poured into iced acid, the organic products extracted with ether, and the extracts washed with sodium carbonate

and dried. The yellow liquids left after removal of the solvents in no case contained benzalacetophenone, for while they reduced potassium permanganate they did not combine with bromine. After standing in an ice chest for several days, the residue obtained by the first procedure partially solidified. The solid was purified by crystallization from methyl alcohol, from which it separated in large colorless prisms, melting at  $78^{\circ}$ .

Analysis:

0.1217 gram substance gave 0.3858 gram  $\text{CO}_2$  and 0.0657 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{13}\text{H}_{12}\text{O}$ .	Found.
C	86.6	86.4
H	5.8	5.9

As the substance has the composition and melting point of a ketophenylhydrindene previously obtained by the action of aluminium chloride on  $\beta,\beta$ -diphenylpropionyl chloride, it was compared with a preparation made in this way and thus identified as 3-keto-1-phenyl-2,3-dihydroindene.

A second product of the reaction was obtained by dissolving the residue from the indene derivative in petroleum ether and cooling the solution in a freezing mixture. After purification this was easily recognized as  $\beta,\beta$ -diphenylpropiophenone, which melts at  $96^{\circ}$ .

The filtrates from ketophenylhydrindene and diphenylpropiophenone contained a substance that decolorized a cold solution of permanganate in acetone, but no solid product could be isolated. The solvents were, therefore, removed and the residual liquid heated under diminished pressure; it lost hydrochloric acid freely above  $150^{\circ}$ , and gave a distillate in which benzalacetophenone was recognized by transformation into its dibromide. This result indicated the presence of  $\beta,\beta$ -chlorphenylpropiophenone in the original product and in all subsequent experiments this substance was isolated by adding to the residues a crystal of a preparation made by direct addition of hydrogen chloride to benzalacetophenone.

All methods of procedure gave variable amounts of the

same three products: ketophenylhydrindene, diphenylpropiophenone and chlorphenylpropiophenone. The presence of a small quantity of the halogen compound is easily explained because it results from direct addition of hydrochloric acid to benzalacetophenone. A number of experiments were made for the purpose of discovering the mechanism by which the other products are formed, but the results are inconclusive. The total amount of these two products formed in any experiment could be estimated with considerable accuracy because they were the only indifferent substances left after the halogen ketone had been destroyed with permanganate. They always constituted 93–95 per cent. of the entire product; but the relative amounts of the two varied within wide limits in experiments in which the conditions were intended to be as nearly as possible the same. Neither was obtained in more than insignificant quantities in all attempts at condensing benzalacetophenone or chlorphenylpropiophenone with benzene in the presence of aluminium chloride.

*Cinnamyl Chloride and Brombenzene.*—The reaction was carried out in carbon bisulphide at  $0^{\circ}$ . In one case ground aluminium chloride was added, in small quantities, to a solution containing cinnamyl chloride and excess of brombenzene, and in another excess of brombenzene was added, gradually, to a suspension of the double compound between cinnamyl chloride and aluminium chloride, but the result of both experiments was essentially the same. The solvent and the excess of brombenzene were removed by distillation with steam and the residual brown paste dissolved in boiling absolute alcohol. This solution, on cooling, deposited a solid that, after a few recrystallizations from alcohol, melted at  $99^{\circ}$ – $100^{\circ}$ .

Analysis:

0.1708 gram substance gave 0.3920 gram  $\text{CO}_2$  and 0.0590 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{15}\text{H}_{11}\text{OBr}$ .	Found.
C	62.71	62.58
H	3.83	3.84



The substance combined with bromine at  $-20^{\circ}$  and rapidly reduced potassium permanganate, being oxidized to benzoic and *p*-bromobenzoic acids. The same substance was readily obtained by adding a small quantity of aqueous potassium hydroxide to an alcoholic solution of equimolecular quantities of benzaldehyde and *p*-bromacetophenone. It is therefore *benzal-p-bromacetophenone*,  $C_6H_5CH : CHCOC_6H_4Br$ . The unsaturated ketone is readily soluble in alcohol, ether, and acetone; sparingly in ligroin. It separates from all of these solvents in pale yellow, friable plates that melt at  $100^{\circ}$ – $101^{\circ}$ .

The reaction with aluminium chloride gave only a small quantity of *benzal-p-bromacetophenone*, the largest yield not exceeding 25 per cent. of the possible quantity. The filtrates from this substance deposited a second product, which was purified by recrystallization from ligroin.

Analysis:

0.1332 gram substance gave 0.3053 gram  $CO_2$  and 0.0463 gram  $H_2O$ .

	Calculated for $C_{16}H_{11}OBr$ .	Found.
C	62.75	62.5
H	3.83	3.9

The substance is isomeric with *benzalbromacetophenone*, but neither reduces permanganate nor combines with bromine. It is, therefore, the corresponding indene derivative.

*6-Brom-3-keto-1-phenyl-2,3-dihydroindene*,



, is readily soluble in all common

organic solvents. It separates from alcohol and from ether in prisms, from ligroin in large, lustrous plates. It melts at  $60^{\circ}$ – $61^{\circ}$ . The yield was 30 to 35 per cent. of the possible quantity.

*Cinnamyl Chloride and Phenol Ethers*.—The experiments of Stockhausen and Gattermann with anisol and phenetol

were repeated under different conditions, but no substance of the type of ketophenylhydrindene and diphenylpropionphenone could be detected in the products; excess of phenol ether does not affect the result in any way and higher temperatures simply lead to decomposition products of the unsaturated ketone. A similar result was obtained with cinnamyl chloride and diphenyl ether. This reaction takes place very slowly, even in direct sunlight, but the yield of unsaturated ketone is excellent, because the aluminium chloride derivative is very sparingly soluble in carbon bisulphide.

*Benzal-p-phenoxyacetophenone*,  $C_6H_5CH : CHCO C_6H_4OC_6H_5$ , is readily soluble in ether and acetone, moderately so in alcohol, sparingly in ligroin. It crystallizes in pale yellow plates that melt at  $85^\circ$ .

Analysis:

0.1571 gram substance gave 0.4794 gram  $CO_2$  and 0.0736 gram  $H_2O$ .

	Calculated for $C_{21}H_{16}O_2$ .	Found.
C	83.97	84.34
H	5.36	5.47

*$\beta$ , $\beta$ -Diphenyl-p-phenoxypropionphenone*,  $(C_6H_5)_2CHCH_2COC_6H_4OC_6H_5$ .—The reaction between phenylmagnesium bromide and benzalphenoxyacetophenone is similar to that between the same reagent and benzalacetophenone; the sole product is a saturated ketone resulting from 1,4-addition. The substance was purified by recrystallization from acetone and alcohol, from which it separated in needles melting at  $103^\circ$ .

Analysis:

0.2107 gram substance gave 0.6604 gram  $CO_2$  and 0.1137 gram  $H_2O$ .

	Calculated for $C_{27}H_{22}O_2$ .	Found.
C	85.71	85.48
H	5.82	5.99

The ketone is readily attacked by bromine but the action of this reagent is not, as usual, confined to the hydrogen in the  $\alpha$  position. Thus, when one molecule of bromine was

added to one of the ketone dissolved in warm chloroform, the solid that separated was found to be a mixture of mono- and dibrom substitution products. A partial separation of the mixture was accomplished by extraction with cold chloroform. The more soluble component, after repeated recrystallization from a mixture of chloroform and alcohol, separated in needles melting at  $163^{\circ}$ – $165^{\circ}$ .

Analysis:

0.1582 gram substance gave 0.4072 gram  $\text{CO}_2$  and 0.0597 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{27}\text{H}_{21}\text{O}_2\text{Br}$ .	Found.
C	70.89	70.19
H	4.62	4.19

The bromine in this compound is in the aliphatic side chain because all of it can be removed by boiling with potassium hydroxide. The substance is, therefore,  $\alpha$ -brom- $\beta,\beta$ -diphenyl-*p*-phenoxypropionophenone.

The residue left after extraction with cold chloroform was recrystallized from boiling chloroform. It separated in minute needles melting at  $211^{\circ}$ – $212^{\circ}$ .

Analysis:

0.1287 gram substance gave 0.2845 gram  $\text{CO}_2$  and 0.0461 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{27}\text{H}_{20}\text{O}_2\text{Br}_2$ .	Found.
C	60.82	60.28
H	3.75	3.97

As only part of the bromine in this compound is eliminated by boiling with bases, the remainder must be located in a nucleus; it is probably in the *para* position of the phenoxy group:  $(\text{C}_6\text{H}_5)_2\text{CHCHBrCOC}_6\text{H}_4\text{OC}_6\text{H}_4\text{Br}$ .

#### *Experiments with Phenyldibrompropionyl Chloride.*

*Preparation of the Chloride.*—We found the method of preparation used by Collet—addition of bromine to cinnamyl chloride—unsatisfactory, because it is extremely difficult to get a product free from unsaturated chloride in this manner. We therefore added bromine to cinnamic acid in the

usual way, suspended the dibromide in phosphorus oxychloride and gradually added a slight excess of phosphorus pentachloride. The resulting chloride could not be distilled without decomposition, but the chlorides of phosphorus were easily removed by heating to  $150^{\circ}$ – $160^{\circ}$  under diminished pressure. The colorless solid obtained in this way can be purified by crystallization from dry carbon bisulphide and ligroin but we found that, in our experiments, the crude and pure preparations gave the same results.

*Action of Aluminium Chloride.*—Our preliminary experiments showed that reactions with phenyldibromopropionyl chloride are accompanied by liberation of bromine. We therefore studied the behavior of this substance in the presence of aluminium chloride alone. For this purpose one molecule of aluminium chloride was gradually added to a solution of the acid in carbon bisulphide that was cooled in a freezing mixture. A slow but steady evolution of gas commenced almost immediately and the color of the solution soon showed the presence of free bromine. The evolution of gas continued for about 24 hours, during which the temperature was allowed to rise, very gradually, to  $15^{\circ}$ . Repeated analyses of the gas showed that, at all stages of the reaction, it consisted of hydrobromic acid mixed with a little hydrochloric acid.

The product of the reaction was poured into iced acid, separated, washed, and dried in the usual way. The ethereal solution was then distilled from a water bath, first under ordinary pressure and finally under 12 mm. The distillate contained, besides carbon bisulphide and ether, a small quantity of phenylacetylene—identified by its copper derivative—and a somewhat larger quantity of bromstyrene recognized by its odor and boiling point. The yellow residue was digested with cold ether. This left a considerable quantity of a sparingly soluble acid, which was purified by recrystallization from boiling acetone and thus obtained in long colorless needles, melting at  $255^{\circ}$ .

Analysis:

I. no. 1799 gram substance gave 0.3134 gram  $\text{CO}_2$  and 0.0481 gram  $\text{H}_2\text{O}$ .

II. 0.1471 gram substance gave 0.2564 gram  $\text{CO}_2$  and 0.0376 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_9\text{H}_7\text{O}_2\text{Br}$ .	I.	Found.	II.
C	47.57	7.51		47.53
H	3.08	2.97		2.84

The sodium salt of the acid was readily oxidized with aqueous permanganate and gave a new acid which melted at  $251^\circ$  and was identified as *p*-brombenzoic acid by comparison with a specimen on hand. The unsaturated acid was therefore *p*-bromcinnamic acid, previously made by Gabriel who gives the melting point  $253^\circ$ .

The filtrates from the *p*-bromcinnamic acid, on dilution with ligroin, deposited a mixture of acids that was finally separated into cinnamic acid, about 20 per cent.,  $\alpha$ -bromcinnamic acid, about 50 per cent., and a small quantity of a new acid that separated from benzene in stout prisms that melted at  $172^\circ$ .

#### Analysis:

I. 0.1733 gram substance gave 0.2552 gram  $\text{CO}_2$  and 0.0422 gram  $\text{H}_2\text{O}$ .

II. 0.1423 gram substance gave 0.2127 gram  $\text{CO}_2$  and 0.0327 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_9\text{H}_8\text{O}_2\text{ClBr}$ .	I.	Found.	II.
C	40.98	40.22		40.75
H	3.03	2.70		2.54

The acid has the composition and chemical properties of an  $\alpha$ -brom- $\beta,\beta$ -phenylchlorpropionic acid; it gives benzoic acid on oxidation with potassium permanganate,  $\alpha$ -bromcinnamic acid and potassium chloride when boiled in alcoholic solution with potassium acetate, and  $\alpha$ -brom- $\beta$ -phenyllactic acid when digested with hot water. The acid is different, however, from the known substance of this composition and structure; it melted  $10^\circ$  lower and a mixture of the two began to melt  $20^\circ$  to  $25^\circ$  below the lower melting component. The ether-ligroin from which all acids had been removed by extraction with sodium carbonate left, after evaporation, a



small quantity of nonacid substances that were not identified.

These results show that aluminium chloride removes both hydrobromic acid and bromine from phenyldibrompropionyl chloride and that action takes place slowly even at the temperature of a freezing mixture. The effect must be due to the phenyl group in the  $\beta$  position, because dibrompropionyl chloride forms a double compound with aluminium chloride which is perfectly stable at the ordinary temperature.

*Phenyldibrompropionyl Chloride and Benzene.*—After trying various methods of procedure, we adopted the following: Sixty grams of ground aluminium chloride were added to a solution of 121 grams of the acid chloride and 50 grams of benzene in 250 cc. of carbon bisulphide. The mixture was kept at  $-20^\circ$  for 24 hours and then poured into iced hydrochloric acid. The carbon bisulphide layer, on evaporation, deposited a solid that was purified by recrystallization from absolute alcohol. It gave 63 grams of a substance that separated in very pale yellow needles melting at  $89^\circ$ – $90^\circ$ . This is evidently the product that had previously been obtained from the same reaction by Collet. Our analysis shows, however, that it is not phenyldibrompropiofenone:

0.1879 gram substance gave 0.4295 gram  $\text{CO}_2$  and 0.0646 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{15}\text{H}_{11}\text{OBr}$ .	Found.
C	62.71	62.33
H	3.83	3.76

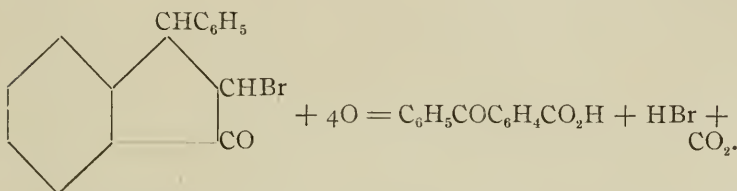
The molecular weight was determined in boiling acetone ( $K = 1710$ ).

Solvent, Grams.	Substance, Grams.	Elevation of boiling point.	Molecular weight.
42.53	0.6274	0.089	285
42.53	1.1752	0.153	285
42.53	1.4925	0.202	262
Calculated for $\text{C}_{15}\text{H}_{11}\text{OBr}$ ,			287

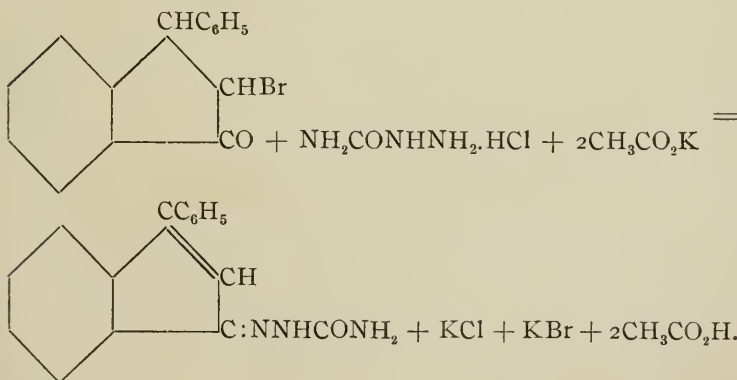
The substance slowly reduced a solution of potassium permanganate in boiling acetone. The sole organic oxidation product was *o*-benzoylbenzoic acid, which was identified by

an analysis, by the melting points of the hydrous and anhydrous acids ( $90^\circ$  and  $120^\circ$ ), and by the melting point of the oxime,  $162^\circ$ .

These results prove that the substance is an indene derivative, the oxidation taking place in accordance with the equation:



*2-Brom-3-keto-1-phenyl-2,3-dihydrindene* reacts readily with organic and inorganic bases, and also with potassium acetate, but it is difficult to isolate pure substances from the products. The substance is most easily identified by means of the semicarbazone obtained by adding an aqueous solution of semicarbazide hydrochloride and potassium acetate to an alcoholic solution of the ketone:



Analysis:

0.1378 gram substance gave 0.3675 gram  $\text{CO}_2$  and 0.0645 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{16}\text{H}_{13}\text{ON}_3$ .	Found.
C	73.0	72.77
H	4.9	5.20

The unsaturated semicarbazone separates in minute yellow needles which, after recrystallization from alcohol and acetone, melt, with decomposition, at  $212^{\circ}$ . The same substance is formed when the yellow oil, obtained by boiling the halogen compound with alcoholic potassium hydroxide, is treated with semicarbazide.

*Phenyldibrompropionyl Chloride and Brombenzene.*—The reaction takes place much more slowly than the corresponding reaction with benzene and consequently leads to the formation of a larger quantity of acid by-products due to the interaction of the acid chloride and aluminium chloride. These acid products were removed by extraction with sodium carbonate. The extracted solution, on dilution with ligroin, deposited a solid which, after repeated crystallization from chloroform and absolute alcohol, melted at  $143^{\circ}$ – $144^{\circ}$ . The substance crystallizes in colorless needles, sparingly soluble in ether and alcohol, readily in acetone.

Analysis:

0.1518 gram substance gave 0.2762 gram  $\text{CO}_2$  and 0.0358 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{15}\text{H}_{10}\text{OBr}_2$ .	Found.
C	49.18	49.55
H	2.70	2.66

The bromine compound reduces potassium permanganate dissolved in acetone—slowly at the ordinary temperature, rapidly near the boiling point of acetone. The sole organic oxidation product is *p*-brom-*o*-benzoylbenzoic acid. This was purified by crystallization from methyl alcohol. It separated in large flat needles or plates melting at  $174^{\circ}$ .

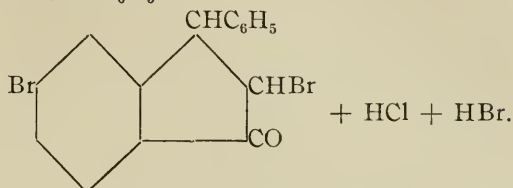
Analysis:

0.1540 gram substance gave 0.3109 gram  $\text{CO}_2$  and 0.0436 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{14}\text{H}_9\text{O}_3\text{Br}$ .	Found.
C	55.08	55.06
H	2.96	3.14

These results prove that the principal product of the reaction between phenyldibrompropionyl chloride and brom-

benzene is 2,6-dibrom-3-keto-1-phenyl-2,3-dihydroindene, an indene derivative with bromine in each nucleus:



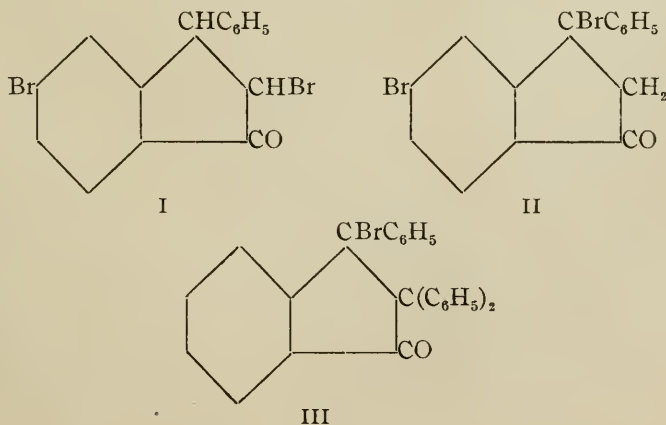
The filtrates from this compound contained another solid product that was isolated with difficulty but finally obtained in large colorless prisms, melting at  $86^\circ$ . This substance was readily soluble in acetone and ether, moderately in alcohol:

Analysis:

0.1834 gram substance gave 0.3334 gram  $\text{CO}_2$  and 0.0409 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{16}\text{H}_{10}\text{OBr}$ .	Found.
C	49.18	49.57
H	2.70	2.47

The substance is isomeric with the product melting at  $143^\circ$  and when oxidized with potassium permanganate it likewise gives brombenzoylbenzoic acid. The two are therefore either stereoisomers due to the presence of two unequal asymmetric carbon atoms, or structural isomers that differ in the position of the bromine atom in the second ring:



Only substances related in this way could be formed in the reaction with brombenzene and also give *p*-brom-*o*-benzoylbenzoic acid on oxidation. Formula II is, however, exceedingly improbable for either of the substances in question because, judging from the observations made with the corresponding triphenylindene derivative (III), the bromine in a compound with this structure would be as reactive as the bromine in triphenylbrommethane. This is not the case. It is much more probable, therefore, that the substances are stereoisomers (I). This conclusion is supported by the ease with which the higher melting is transformed into the lower melting substance by heating. A perfectly clean and almost complete transformation is obtained by keeping it at its melting point for an hour.

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## THE EQUILIBRIUM BETWEEN AMMONIUM BENZOATE AND BENZAMIDE AND WATER.

BY E. EMMET REID.

Acetamide has long been prepared by distilling, or otherwise heating, ammonium acetate. Hofmann<sup>1</sup> prepared a number of aliphatic amides by heating the ammonium salts of the corresponding acids. He obtained yields running up to about 80 per cent., particularly for the amides of higher molecular weights. Menshutkin<sup>2</sup> and later Goldschmidt<sup>3</sup> studied the formation of anilides, both as to rate and limit. Both of these investigators concluded that the formation of anilides is analogous to esterification. Menshutkin found well-defined limits for the formation of the anilides and, in a later paper,<sup>4</sup> took up the question of the formation of amides. He prepared pure ammonium salts and heated specimens of these in sealed tubes and estimated the amount of ammonium salt remaining by titration of the acid of the ammonium salt in strong alcohol solution, in which ammonia does not

<sup>1</sup> Ber. d. chem. Ges., **15**, 977.

<sup>2</sup> *Ibid.*, **15**, 1615. J. prakt. Chem., [2] **26**, 208.

<sup>3</sup> Z. physik. Chem., **24**, 353.

<sup>4</sup> J. prakt. Chem., **29**, 422, 436.



affect phenolphthalein. He used ammonium salts of acids from formic to caproic and also benzoic and anisic acids. With the salts of the aliphatic acids good results were obtained, showing that a limit is reached in each case, that the limit varies somewhat with the temperature, and that it varies with the acid. At  $155^{\circ}$ , the limit rose rather regularly from 81.46 per cent. of amide for acetic acid, to 84.33 per cent. for caproic acid. He did not try the influence of excess of acid or of ammonia and did not make any attempt to reach the limit from the other end, that is, from a mixture of amide and water.

With the ammonium salts of benzoic and anisic acids he got almost no amide formation, ammonium benzoate giving him, at  $155^{\circ}$ , 6.70 per cent. of amide in 240 hours and 8.82 per cent. in 288 hours. His results, though excellent for the fatty acids, did not settle the question for the aromatic series.

In connection with a study of the esterification of benzamide by alcohol and mercaptan it became of interest to know the location of the corresponding limit with water, hence the following preliminary study was undertaken:

*Materials.*—The benzamide used was made from benzoyl chloride and ammonia. It was crystallized twice from water, once from alcohol, once from dilute ammonia, again from water, and finally from conductivity water. The ammonium benzoate was made from Kahlbaum's best benzoic acid and ammonia, and dried in the air. As it was found to lose ammonia and not to be constant in composition the ammonia content of each sample was determined. Conductivity water was used in the experiments with the amide.

*Method of Work.*—The benzamide and water, or the ammonium benzoate, as the case might be, were weighed into small hard glass tubes which had been well extracted with dilute hydrochloric acid before use. The mixture about half filled the tubes. They were heated exactly as in the experiments with benzoic acid and mercaptan.<sup>1</sup> After opening and breaking, the tubes and their contents were placed quickly in the stills. The ammonia was estimated by distillation with mag-

<sup>1</sup> THIS JOURNAL, 43, 489.

Table I.—Benzamide and Water.

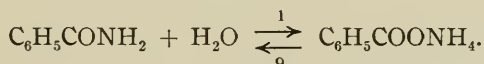
Time in hours	41	41	60	64	64	64
Temperature	180-220°	180-220°	170-220°	200-220°	200-220°	200-220°
Wt. amide	0.3633	0.3633	0.3633	0.4110	0.5439	0.3677
Wt. water	0.0522	0.0868	0.1102	0.1019	0.1125	0.0548
Amide (millimoles)	3.000	3.000	3.000	3.391	4.491	3.036
Water (millimoles)	2.897	4.817	6.115	5.656	6.245	3.042
Ammonia found (millimoles)	0.792	0.950	1.169	1.085	1.243	0.866
Amide left (millimoles)	2.208	2.050	1.831	2.306	3.248	2.279
Water left (millimoles)	2.105	3.867	4.946	4.571	5.002	2.285
$\eta$	7.410	8.804	6.627	8.562	10.515	9.087
$\sqrt{\eta}$	2.722	2.967	2.574	2.926	3.243	3.015
Per cent. ammonium salt at limit	26.87	25.21	(27.98)	25.47	23.57	24.91
						24.47

nesium hydroxide and allowance was made for the small amount of amide thus decomposed.<sup>1</sup> In the case of the ammonium benzoate samples, the amide remaining was estimated by decomposition with strong caustic soda. From the total ammonia thus found, the ammonium benzoate in the original sample was estimated and the balance of the sample considered as benzoic acid.

The results are given in the above table. The units are the same and the results were calculated according to the same plan as used in the above mentioned paper on benzoic acid and mercaptan.

In the third experiment the temperature for the last 19 hours was 170°–180°. This indicates that at lower temperatures the limit for the formation of amide from ammonium salt is lower.

The average, excluding the third experiment, is 25.17 per cent., which means that a mixture of equivalent amounts of benzamide and water, when heated to 200°–220°, is one-fourth transformed into ammonium benzoate, or that the initial rate of amide formation is nine times as great as that of its decomposition. Or writing the equation as reversible and using the notation introduced in the above mentioned paper on benzoic acid and mercaptan, we have:



*Table II.—Ammonium Benzoate.*

Time in hours	70	70
Temperature	200–220°	200–20°
Original acid (millimoles)	2.898	2.787
Original ammonia (millimoles)	2.886	2.808
Acid at limit (millimoles)	0.674	0.715
Ammonia at limit (millimoles)	0.662	0.694
Benzamide-water (millimoles)	2.224	2.093
$r$	11.09	8.828
$\sqrt{r}$	3.245	2.971
Per cent. of ammonium salt at limit	23.56	25.18
Average		24.4

<sup>1</sup> THIS JOURNAL, 41, 486.

These results, being in substantial agreement with those found starting from the other end, show that the reaction is strictly reversible and that the limit may be easily reached from either end. The variation of the individual results may be, in part, attributed to the fact that the temperatures were not regulated, for Menshutkin found a variation of the limit with a change of temperature. It will be noticed that the limit as found is substantially the same with varying proportions of the constituents.

Benzoic acid, contrary to Menshutkin's few observations, is shown to be in line with the acids of the aliphatic series. The rather low temperature at which he tried the ammonium benzoate may be the reason for his poor results on that salt.

JOHNS HOPKINS UNIVERSITY,  
BALTIMORE, MD.,  
April 28, 1910.

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## FRICITION IN THE BOMB CALORIMETER.

BY H. A. ROESLER.

The heating effect due to the friction of the stirrer in the bomb calorimeter is generally supposed to be very small, but in connection with some calculations relative to the rate of radiation in the calorimeter certain discrepancies were found which could only be explained by the addition of considerable heat from the friction of the stirring apparatus, and a method for determining this heating effect was therefore evolved.

The object of this article is to show how the heat of friction, its magnitude under different conditions, and its relation to the calculation of the radiation correction may be accurately determined.

The rise in temperature during the initial period is due to the algebraic sum of the heat absorbed or evolved by radiation and the heat added by the stirring apparatus.

Let  $S$  = rate of rise in temperature due to radiation plus friction.

$V$  = rate of rise in temperature due to radiation alone.

$F$  = rate of rise in temperature due to friction.

$M$  = temperature of the calorimeter.

$M'$  = temperature of the surrounding medium.

$t$  = difference between the temperature of the calorimeter and that of the surrounding medium.

$r$  = rate of rise in temperature per degree difference in temperature ( $t$ ) due to radiation.

This value of  $r$  may be termed the radiation constant of the calorimeter. It is obtained by dividing the rate of rise in temperature by the difference in temperature of the calorimeter and the surrounding medium.

Then:

$$V = rt.$$

$$F = S - V = S - rt.$$

$$t = M' - M.$$

Two values of  $S$ ,  $S_1$  and  $S_2$  are now determined at temperature differences  $t_1$  and  $t_2$ . Then we have:

$$\frac{S_1 - S_2}{t_1 - t_2} = \frac{(V_1 + F) - (V_2 + F)}{t_1 - t_2} = \frac{V_1 - V_2}{t_1 - t_2}.$$

But since  $\frac{V_1}{t_1} = r$  and  $\frac{V_2}{t_2} = r$ , then  $\frac{V_1 - V_2}{t_1 - t_2} = r$ .

Therefore,

$$F = S_1 - rt_1 = S_1 - \left( \frac{S_1 - S_2}{t_1 - t_2} \right) t_1.$$

The value of  $F$  is most accurately determined when one value of  $t$  is nearly zero and the other is several degrees above or below or when one is positive and the other negative.

A number of sets of determinations for  $S$  and  $t$ , one of which is shown below for the purpose of illustration, were made on the calorimeter used in this laboratory. The values for  $S$  were obtained by taking 10 consecutive readings at intervals of one minute and averaging. The temperature of the calorimeter was then raised about 0.5 of a degree by means of a small iron wire coil, immersed directly in the water and heated electrically, and  $S$  was again determined in the same manner. In order to keep conditions as nearly uniform as possible, the calorimeter is surrounded by a water jacket, a double lid



placed over the top and a felt covering one inch thick fitted over all. The stirrer is of the propeller type, the shaft, to which is attached the pulley, projecting out from the top of the calorimeter.

The results obtained are as follows:

Reference No.	Average, $M'$ .	Average, $M$ .	$t$ .	Average, $S$ .
1	23°.013	18°.544	4°.469	0°.0128
2	22°.987	19°.065	3°.922	0°.0112
3	22°.966	19°.576	3°.390	0°.0099
4	22°.947	20°.061	2°.866	0°.0089
5	22°.933	20°.556	2°.377	0°.0079
6	22°.928	21°.046	1°.822	0°.0067
7	22°.939	21°.504	1°.435	0°.0055
8	22°.943	21°.987	0°.956	0°.0047
9	22°.964	22°.525	0°.439	0°.0036
10	22°.980	22°.796	0°.184	0°.0029
11	22°.981	22°.825	0°.156	0°.0029
12	22°.996	23°.007	—0°.011	0°.0024
13	23°.006	23°.026	—0°.020	0°.0023
14	23°.016	23°.049	—0°.033	0°.0023

Taking various combinations of  $S$  and  $t$  and calculating  $F$ , we get:

Reference No.	$F$ .	Reference No.	$F$ .
1 and 14	0°.0024	3 and 14	0°.0024
1 and 13	0°.0023	3 and 13	0°.0023
1 and 12	0°.0024	3 and 12	0°.0024
1 and 11	0°.0025	3 and 11	0°.0026
1 and 10	0°.0025	3 and 10	0°.0025
1 and 9	0°.0026	3 and 9	0°.0027
2 and 14	0°.0024	4 and 14	0°.0024
2 and 13	0°.0023	4 and 13	0°.0023
2 and 12	0°.0024	4 and 12	0°.0024
2 and 11	0°.0026	4 and 11	0°.0026
2 and 10	0°.0025	4 and 10	0°.0025
2 and 9	0°.0026	4 and 9	0°.0026

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Average, 0°.0025

Thus  $F$  is found to be constant for almost any combination of  $S$  and  $t$ , provided the values for  $t$  are several degrees apart.

When  $F$  is calculated from the readings taken in an ordinary calorific determination the same result is obtained:

Lab. No.		Av. $M'$ .	Av. $M$ .	$t$ .	$S$ .	$F$ .
26627	Initial period	20°.940	19°.319	+1°.621	+0°.0065	
	Final period	20°.950	22°.017	—1°.067	+0°.0000	0°.0026
26628	Initial period	21°.070	19°.577	+1°.493	+0°.0067	
	Final period	21°.115	22°.282	—1°.167	+0°.0000	0°.0029
26629	Initial period	21°.625	19°.865	+1°.760	+0°.0075	
	Final period	21°.655	22°.557	—0°.902	+0°.0002	0°.0027
26630	Initial period	21°.805	19°.655	+2°.150	+0°.0080	
	Final period	21°.830	22°.344	—0°.514	+0°.0012	0°.0026
26631	Initial period	20°.270	19°.620	+0°.650	+0°.0042	
	Final period	20°.320	22°.236	—1°.916	—0°.0022	0°.0026

The water equivalent of the calorimeter from which these data were taken is 2944 grams, therefore the friction was adding to the apparatus  $2944 \times 0.0024 = 7.1$  calories per minute. During the whole combustion period of 6 minutes this would be  $6 \times 7.1 = 42.6$  calories.

The value for  $F$  obtained on another calorimeter which was equipped with the Mahler stirrer was 0°.005. This instrument has a water equivalent of 2767 grams, which gives 13.8 calories per minute for friction or 82.8 calories for the whole combustion period.

This is much larger than would be suspected but it is taken into account in the correction for radiation, as shown below. It emphasizes, however, the necessity of having an absolutely uniform rate of stirring. The author found upon one occasion that even the loosening of the belt reduced the friction almost 50 per cent.

The best motor to employ is an alternating current induction fan motor. A direct current motor is not so desirable because changes in the voltage will also vary the speed. Stirring by hand should not be attempted if it is possible to obtain a motor, because experience has shown that it is impossible to stir continuously for 20 minutes and maintain a constant speed.

The relation of the friction to the correction for radiation may be shown as follows:

The formula used for the calculation of the radiation correction is that of Regnault-Pflaunder,

$$C = nV + \frac{V' - V}{\theta' - \theta} \left( \frac{\theta_0 + \theta_n}{2} + \sum_1^{n-1} \theta - n\theta \right),$$

where

$n$  = number of minutes in the combustion period.

$V$  = rate of rise in temperature during the initial period.

$V'$  = rate of rise in temperature during the final period.

$\theta$  = mean temperature of the calorimeter during the initial period.

$\theta'$  = mean temperature of the calorimeter during the final period.

$\theta_1, \theta_2, \dots, \theta_n$  = temperature at the end of the first, second, . . . . .  $n$ th, minutes of the combustion period.

$\theta_0$  = temperature at the moment of ignition.

In practice we do not get the values  $V$  and  $V'$ , but  $V + F$  and  $V' + F$ . If, then, these values be substituted in the formula in the place of  $V$  and  $V'$  we find that the value of  $C$  has been increased to that of  $C + nF$ . That is, we get the identical result which would be obtained if we used the true values of  $V$  and  $V'$  and then added to the value of  $C$  thus obtained the correction for the rise in temperature,  $nF$ , caused by the friction during the combustion period.

The magnitude of  $F$  does not, therefore, effect the accuracy of a calorific determination provided it is uniform throughout the whole time of the determination.

LABORATORY OF THE CONSOLIDATION  
COAL CO., INC.

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## NOTE.

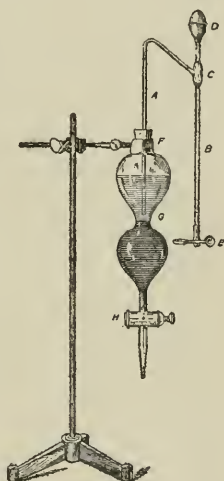
### A SEPARATORY APPARATUS.

The accompanying cut illustrates a separatory apparatus which we find to be a valuable adjunct to our laboratory equipment. It consists of a double bulbed separatory funnel and a pipette siphon, the latter having been fully described in the June number of *The Journal of the American Chemical Society* of this year.

The advantages of this form of separatory funnel are: First,

it allows of a better and more rapid extraction, for upon inverting the funnel the solvent and solution must pass each other at the constriction *G*, thus permitting more intimate contact of the two liquids. Second, when it is desired to siphon off the top layer in the funnel, the surface of the last portions siphoned is reduced to that in the constriction, thus allowing a more perfect separation. Third, emulsions do not form so readily when the space is constricted like that at *G*, and when they do form, they are more easily destroyed than in the ordinary funnel. Fourth, when three layers are formed the middle layer may be completely removed by means of the siphon without disturbing the other two.

A cork is fitted to the branch *A* of the siphon so that its position may be raised or lowered during the process of siphoning. To operate the siphon: Open the spring clamp *E*, compress the rubber bulb *D*, close the lower end of *B* by releasing the pressure on the spring clamp, slowly release the pressure on the rubber bulb, and the liquid will be drawn into the siphon, filling both arms and part of the bulb *C*. Then open clamp *E* and the liquid siphons over.



When it is desired to filter the siphoned liquid, the two processes may be made to go on simultaneously, by supporting the filter so that the siphoned liquid will run into it, and holding open the spring clamp by means of a chip of wood, so that the drip from the siphon equals that from the filter.

The siphon may also be used to advantage for removing supernatant liquids where decantation is found to be impracticable, for drawing off standard solutions, reagents and liquids with offensive and poisonous vapors, etc.

NEVADA AGRICULTURAL EXPERI-  
MENT STATION.

C. A. JACOBSON and  
S. C. DINSMORE.

## REPORT.

### CHEMICAL CONSTITUTION AND THE ABSORPTION OF LIGHT.<sup>1</sup>

#### *A Method of Chemical Analysis.*

Research along many lines in science is often very much

<sup>1</sup> This report is based upon an article by H. Ley, entitled "Ueber die Beziehung zwischen Lichtabsorption und chemischer Konstitution bei organischen Verbindungen." See *Jahrbuch der Radioaktivität und Elektronik*, 6, 274 (1909).

stimulated by the requirements of technology. This is especially true in connection with many branches of organic chemistry and a good example is furnished by the pure food laws. In regulating the use of various coloring and preserving matters added to foods, it is necessary that the examiners shall be able to recognize various compounds easily and quickly. Many organic compounds possess very characteristic colors and it has often been asked whether the absorption spectra of these compounds would aid in their analysis. Our present knowledge of absorption spectra is mostly limited to the visible region of the spectrum. Before this method of analysis can reach its full service to chemists it will be necessary to measure the absorption throughout the region of the infrared. At present the absorption spectra of a few potassium salts have been explored to regions of wave lengths as long as 0.1 mm. (Electromagnetic waves having wave lengths between 8000 m. and 6 mm. have been produced.)

The analysis of inorganic compounds is probably less hopeful, although the absorption spectra would often help to identify compounds. A great many of the inorganic cations show characteristic absorption in the visible portion of the spectrum and practically all have bands in the infrared. J. Formanek<sup>1</sup> has suggested that the presence of metals in metallic compounds of alkannin could be determined from the absorption spectra of these compounds. The following measurements of the absorption bands of the different compounds of alkannin show the effect of the metal upon the position of the bands:

	$\lambda$ .	$\lambda$ .	$\lambda$ .
Uranium	6870	6315	....
Iron	6545	6030	....
Potassium	6387	5910	....
Cobalt	6370	5845	5405
Sodium	6337	5857	....
Barium	6281	5805	5395
Lithium	6210	5745	5340
Nickel	6192	5725	5320
Calcium	6147	5682	5276
Copper	5953	5515	5128
Aluminium	5857	5425	5048

The use of absorption and emission spectra has been very successful in studying the elements of the rare earths and has been very extensively applied by Crookes, Becquerel, Exner, Demarçay, and many others. An account of this work is

<sup>1</sup> Die qualitative Spectralanalyse anorganischer Körper.



given by Böhm.<sup>1</sup> Recently Urbain<sup>2</sup> has employed the phosphorescent spectra in the purification of compounds of europium, gadolinium, terbium, dysprosium, neoytterbium and lutecium.

*Atomic Structure and Spectra.*

The greatest interest lies, however, in the relation between chemical constitution and absorption or emission spectra. The relation between flame, spark and arc spectra and the chemistry of the emitters is not known. The source of spectra like that from the blue cone of a Bunsen burner, the Swan spectra, is at present a much mooted problem. It is probable that chemical reactions play an important rôle in the emission and absorption of spectra, and especially of band spectra. We usually think of most spectrum lines like  $D_1$  and  $D_2$  of sodium as coming from the metallic atoms. Fredenhagen<sup>3</sup> points out that under most conditions oxygen is present. In chlorine, hydrogen or fluorine flames, calcium, strontium, thallium, sodium, barium and copper emit spectra that are very different from those obtained when oxygen is present. Under these conditions thallium does not emit the characteristic green line and the lines  $D_1$  and  $D_2$  are completely absent. Work on the absorption of sodium, mercury, potassium and various other vapors show that the presence of foreign gases modifies the character of the absorption very much. Many believe that certain series or groups of lines are due to chemical reactions of various kinds.

Chemical reactions and processes of ionization and recombination are believed to place the atom or molecule in a peculiar condition, in which it can emit energy to the ether or absorb energy from it. Under ordinary conditions the atom does not seem capable of doing this. In sodium vapor, for instance, according to present theories only one atom in thousands is taking part in absorption at any one time. The problem as to how energy is transferred to and from matter is one of the most fundamental problems of science. A striking example of the fact that a few atoms under peculiar conditions have the power of absorbing an enormous amount of energy from the ether is exhibited by the iron absorption lines in the solar spectrum. An arc of carbon electrodes containing iron as an impurity emits enough iron vapor to absorb as much as the iron vapor in the sun. It is thus seen that an infinitesimal amount of iron in the very great atmosphere

<sup>1</sup> Die Darstellung der seltenen Erden, Leipzig, 1905.

<sup>2</sup> Le Radium, June, 1909.

<sup>3</sup> Physik. Z., Oct. 24, 1907.

of the sun is sufficient to absorb a large part of the energy emitted by the photosphere.

Our present theory of the mechanism of the absorption and emission of radiations is very simple. Light and heat are electromagnetic radiations and hence the emitter and the absorber must either be an electric charge or a magnetic pole. As free magnetic poles are unknown to us while free electric charges are known, this theory makes the electric charge the origin of all electromagnetic phenomena. At present no positive electric charges are known to be associated with portions of matter smaller than the hydrogen atom. On the other hand, negative electrons are known to be associated with masses only about one two-thousandth that of the hydrogen atom. As far as experiment shows, these electrons always have the same properties and the same charge (the charge is invariably considered as constant when  $e/m$  varies), no matter from what element they may come. It is for these reasons that the electron is made the basis of all electromagnetic theory and at present there are but few phenomena capable of any explanation which cannot be explained by this theory.

Electromagnetic radiations then have their origin in electric charges. Continuous spectra (as from hot metals) are due to free electrons and these apparently have very little connection with the chemical constitution of the metal molecules. Fine line and band spectra are apparently due to different systems of electrons within the atom and are greatly affected in intensity by the presence of neighboring atoms. The electrons of this type vibrate in definite frequencies that can be changed only very slightly by changing the external conditions.

#### *The Absorption Spectra of Organic Compounds.*

*The Unit of this Absorption.*—In discussions concerning the color of organic compounds it is customary to speak of the selective absorption as being due to certain ions or molecules. This is probably true in the infrared; the electric charges absorbing these long wave length radiations are probably associated with masses of molecular size. But in the visible and ultraviolet portions of the spectrum the value  $e/m$  of the absorbers is invariably of the same magnitude as that of the electron. Drude<sup>1</sup> has investigated a large number of organic compounds and shows that the absorber of all the shorter waves of the spectrum is the negative electron. Houstoun<sup>2</sup>

<sup>1</sup> Ann. Physik, **14**, 677, 726, 936, 961 (1904).

<sup>2</sup> Nature, May 20, 1909. P. Roy. Soc., **82**, A, 606 (1909).

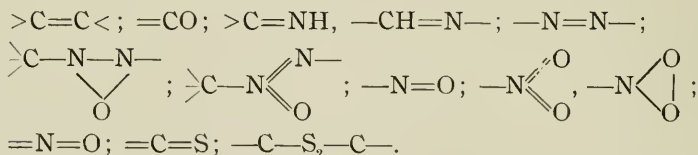
has calculated the value of  $e/m = 1.297 V K \frac{\lambda_1 - \lambda_0}{\lambda_0^3}$  for the absorption bands of several organic compounds and also shows that the absorber is the electron ( $V$  is the refractive index,  $K$  the maximum value of the coefficient of extinction;  $\lambda_0$  is the wave length of maximum absorption, and  $\lambda_1$  is the wave length for which the coefficient of extinction has a value equal to half its maximum. The formula used is based on the present theories of dispersion). The following table is from Houstoun:

Compound.	$\lambda_0$ .	$e/m$ .
Fuchsin in alcohol	5500	1.8(10) <sup>7</sup>
Phloxin in water	5150	1.4 "
Crystal violet in alcohol	5750	4.9 "
Corallin in alcohol	4650	1.6(10) <sup>6</sup>
Methylene blue in water	6650	5.4 "
Water blue in water	5750	8.1 "
Eosin in water	5150	6.9 "
Cyanine in alcohol	5870	5.8 "

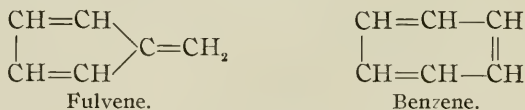
Throughout the present paper the absorbers are considered as negative electrons. These electrons have certain free periods corresponding to the bands of selective absorption. These free periods are greatly modified by the presence of certain chemical radicals and seem to be electrons that are situated either in the outer parts of the atom or between two or more atoms. Stark and others call these the valency electrons and consider that chemical valency is due to them. Chemical bonds will then be closely associated with the electric fields of these electrons. While the theory in its present state is confronted with many difficulties, yet it seems a step towards the explanation of the more or less vague chemical bond. As an aid to our imagination, we shall consider atoms or ions as large spherical regions throughout which a positive charge is uniformly distributed. These regions are sometimes spoken of as "spheres of influence." Two atoms collide when their "spheres of influence" touch. Groups of atoms composing ions, radicals or molecules, will have "spheres of influence." No ion can penetrate the sphere of influence of another atom or molecule. On the other hand, the electrons are very small and bear much the same relations in size to the atom that the sun bears to the solar system. The electric fields of the electrons occupy quite large volumes, however, although the energy of this field is mostly situated in a very small space. Electrons can therefore move through

ions and atoms if they have sufficient velocity. In most organic compounds it is considered that the valency electrons move in the interatomic spaces with considerable ease. In the metals a large number of the electrons are free. In organic compounds that are transparent to certain wave lengths, the electrons in general will be held within certain regions by forces which are supposed to be elastic in their nature.

*The Theory of Chromophores.*—In considering absorption spectra it is often quite sufficient to speak qualitatively of the color of different compounds. The introduction of certain groups into colorless compounds often results in a colored compound. Any such group is a chromophore. Sometimes the chromophore may be weak and it may require the addition of several chromophores to produce a colored compound. Ultimately the color is due to absorbers existing in the chromophore—probably the valency electrons. Among the better known chromophores are the groups:

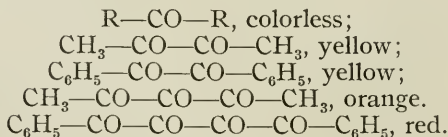


The ethylene group,  $>C=C<$ , is a weak chromophore and several chromophores must be present before the absorption is sufficient to produce color. An example is that of fulvene and its isomer, benzene:



Benzene is colorless and exhibits absorption only in the ultraviolet, whereas fulvene is an orange-yellow.

The carbonyl group,  $=C=O$ , is also weak and several of the groups must be present in a compound to produce color. The following examples indicate how an increasing number of the carbonyl groups produces a greater and greater absorption of the shorter wave lengths:

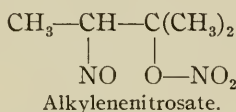
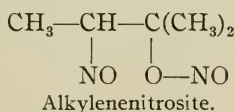


The combination of two phenyl groups causes absorption only in the ultraviolet. The introduction of the  $-\text{CH}=\text{N}-$  chromophore is sufficient to produce color, as is shown in the yellow benzylidenaniline,  $\text{C}_6\text{H}_5\text{CH}=\text{N}-\text{C}_6\text{H}_5$ . The azo chromophore,  $-\text{N}=\text{N}-$ , produces the same effect, as shown in the orange azobenzene,  $\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$ . The chromo-

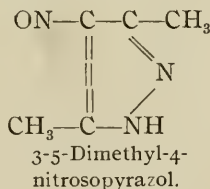
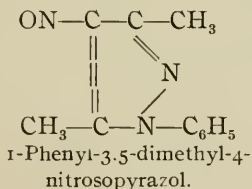
phores  $\text{>C}-\text{N}-\text{N}-$  and  $\text{>C}-\text{N}=\text{N}-$ , on the other hand,

are very weak.

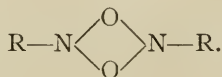
The nitroso group,  $-\text{N}=\text{O}$ , is a very strong chromophore when it is joined to a carbon atom directly. The effect of this chromophore is shown in nitrosobenzene,  $\text{ON}-\text{C}_6\text{H}_5$ , which is of a green color. Wallach,<sup>1</sup> and recently J. Schmidt,<sup>2</sup> have investigated the following compounds, which are of a deep blue color:



According to Wolff,<sup>3</sup> the following nitroso compounds, the first of which is green and the second blue, have the structures:



The carrier of the color in these cases is the  $\text{C}-\text{N}=\text{O}$  group. Many of the aliphatic nitroso compounds show polymerization and are then often colorless. The polymerization of  $\text{R}-\text{N}=\text{O}$  to  $(\text{RNO})_2$  is probably accompanied by a rearrangement as follows:



This would explain why the polymer is colorless.

<sup>1</sup> Ann. Chem. (Liebig), **241**, 288; **322**, 305.

<sup>2</sup> Ber. d. chem. Ges., **35**, 2323, 3721; **36**, 1768.

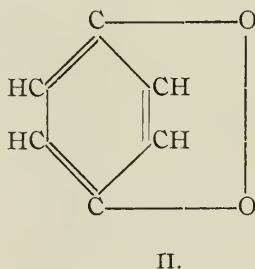
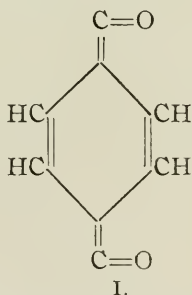
<sup>3</sup> Ann. Chem. (Liebig), **325**, 192.



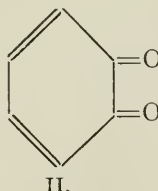
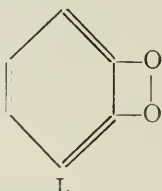
The nitro group  $\text{—N} \begin{smallmatrix} \diagup \text{O} \\ \diagdown \text{O} \end{smallmatrix}$  or  $\text{—N} \begin{smallmatrix} \diagup \text{O} \\ | \\ \diagdown \text{O} \end{smallmatrix}$  is a very weak chromophore. The aliphatic nitro compounds,  $\text{CH}_3\text{NO}_2$ ,  $\text{C}_2\text{H}_5\text{NO}_2$ , etc., are colorless. When combined with other chromophores, colored compounds, such as nitrobenzene or nitronaphthalene, can be obtained. Stobbe<sup>1</sup> has investigated the influence of the nitro group on the fulgides. In solution the *p*-nitrophenylfulgide has a deep red color. The ortho and meta compounds are much less deeply colored.

Hantzsch<sup>2</sup> and Raschig<sup>3</sup> have shown that the  $\text{=N=O}$  group acts as a chromophore in the sulphonate,  $\text{O=N=(SO}_3\text{K)}_2$ , which is violet in solution and orange in the solid state. The thiocarbonyl group,  $\text{=C=S}$ , is a rather strong chromophore. Examples are the blue compounds thioacetophenone,  $\text{C}_6\text{H}_5\text{—CS—CH}_3$ , and thiobenzophenone,  $\text{C}_6\text{H}_5\text{—CS—C}_6\text{H}_5$ . For a fuller account of the color properties of various compounds, the reader is referred to Ley's paper,<sup>4</sup> from which the data here recorded have been largely taken.

There has been a great deal of discussion whether quinone has the formula I or II:



Willstätter and F. Müller<sup>5</sup> have found that *o*-benzoquinone can exist in two forms, I and II, the former being colorless and the latter red:



<sup>1</sup> Ber. d. chem. Ges., **38**, 4082 (1905).

<sup>2</sup> *Ibid.*, **28**, 2744.

<sup>3</sup> Dammer: Handb. d. anorg. Chem.

<sup>4</sup> Jahrb. d. Rad. u. Elek., **6**, 274–381 (1909).

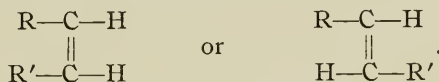
<sup>5</sup> Ber. d. chem. Ges., **41**, 2580 (1908).

This fact may possibly explain several outstanding difficulties among quinone derivatives. It would be expected that the substitution of an (NR) group for oxygen in a quinone would give a deeply colored substance. As a matter of fact, quinonediphenylimide,



is brownish red. But the compounds  $\text{NH} : \text{C}_6\text{H}_4 : \text{NH}$  and  $\text{O} : \text{C}_6\text{H}_4 : \text{NH}$  are colorless. This can easily be explained if the latter compounds are assumed to have the superoxide formula similar to that of *o*-benzoquinone. The quinone chromophore enters into the composition of quite a large number of colored compounds.

The space relations of the chromophores seem to affect the color of compounds. For instance, the ethylene group can have two isomeric configurations:



This geometric isomerism may explain the following facts:

1. Diethoxynaphthostilbenes,  $\text{C}_2\text{H}_5\text{O}-\text{C}_{10}\text{H}_6\text{CH} : \text{CH} \cdot \text{C}_{10}\text{H}_6 \cdot \text{OC}_2\text{H}_5$ .<sup>1</sup> The form which has the highest melting point is colorless, while the lower melting form is yellow.

2. Dibenzoylthylenes,  $\text{C}_6\text{H}_5\text{CO} \cdot \text{CH} : \text{CH} \cdot \text{COC}_6\text{H}_5$ .<sup>2</sup> The higher melting form is colorless, while the lower melting form possesses a deep yellow color.

That the color producing power of the chromophores is due to the double bonds seems quite certain. When these bonds are saturated the resulting compounds are colorless.

Colored.

$\text{C}_6\text{H}_5-\text{N}=\text{N}-\text{C}_6\text{H}_5$ , azobenzene.

$\text{C}_6\text{H}_5-\text{N}=\text{O}$ , nitrosobenzene.

$\text{O} = \text{C}_6\text{H}_4 = \text{O}$ , quinone.

$\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CO} \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , diphenyltriketone.

Colorless.

$\text{C}_6\text{H}_5\text{NH}-\text{NHC}_6\text{H}_5$ , hydrazobenzene.

$\text{C}_6\text{H}_5-\text{N} \cdot \text{H} \cdot \text{OH}$ , phenylhydroxylamine.

$\text{HO} \cdot \text{C}_6\text{H}_4 \cdot \text{OH}$ , hydroquinone.

$\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{CO} \cdot \text{C}_6\text{H}_5$ , dibenzoylmethane.

<sup>1</sup> Elbs: J. prakt. Chem., **47**, 72.

<sup>2</sup> Paal and Schulze: Ber. d. chem. Ges., **33**, 8795; **35**, 168.

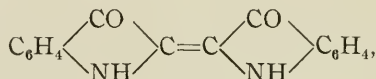
The different di- and tri-substitution products usually give rise to different absorption bands when the absorption is selective. Ortho- and metaxylene have one band, whereas paraxylene has two. The following gives the value of the limit of absorption when light is passed through a gram molecule of the substance.

	Cresol.	Dihydroxybenzene.	Hydroxybenzoic acid.
Meta	3433	3466	3359
Ortho	3413	3399	3080
Para	3359	3151	2986

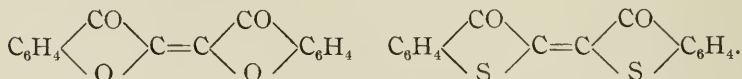
When a chromophore is introduced into a compound the bands may be shifted towards the red or towards the violet. The former effect is bathochromous, the latter hypsochromous. The effect of joining chromophores is usually bathochromous. For example:

	$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .
Benzene	2610	2540	2450	2440
Naphthalene	2850	2720	2630	2550
Anthracene	...	3600	3430	3280

In triphenylmethane the limit of the visible portion of the spectrum is reached. It may be stated here that anthracene and phenanthrene have entirely different absorption spectra, although the fluorescent spectra are very similar.<sup>1</sup> An auxochrome is a radical that causes the absorption to be more intense. An example is  $\text{—CO—C=C—CO—}$ , which appears in the indigos,



and also in the deeply colored compounds:



The groups  $\text{CH}_3$ ,  $\text{OCH}_3$ ,  $\text{C}_2\text{H}_5$ , the halogens, etc., are bathochromes, while the groups  $\text{NO}_2$  and  $\text{NH}_2$  are hypsochromes.

The infrared absorption spectra to about  $15\mu$  of a large number of organic compounds have been investigated by W. W. Coblentz.<sup>2</sup> Isomeric compounds are found to possess very different absorption, depending on the bonding of the atoms in the molecule. Stereomeric compounds, on the

<sup>1</sup> Elston: *Astrophysical J.*, **25**, 3 (1907).

<sup>2</sup> Investigations of Infrared Spectra, Carnegie Publication No. 35.

other hand, were found to possess the same absorption spectra. The replacing of hydrogen by an  $\text{NH}_2$  or  $\text{CH}_3$  group usually results in the appearance of new bands. In the spectrum of certain benzene derivatives, however, the benzene spectrum is usually present. The carbohydrates investigated had characteristic spectra with absorption bands at  $0.83$  to  $0.86\mu$ ;  $1.67$  to  $1.72\mu$ ;  $3.25$  to  $3.43\mu$ ;  $6.75$  to  $6.86\mu$ ; and  $13.6$  to  $14\mu$ . The three isomeric xylenes have banded spectra in which the most important line in each group lies farthest toward the long wave lengths in the order ortho, meta, and para.

The author<sup>1</sup> has shown that the effect of the  $\text{NO}_3$  group and of free nitric acid is hypsochromous, causing the uranyl bands to shift towards the violet. The effect of free hydrochloric acid or of zinc, aluminium or calcium chlorides on the uranyl chloride bands is bathochromous. Recently the author has found that the  $\text{NO}_3$  group is hypsochromous with respect to the neodymium and erbium bands.

*Influence of the Solvent.*—Theoretically it would be expected that the position of the absorption bands would be different for different solvents. Kundt's rule that the bands should be shifted to the red as the refractive index increases does not hold. It is usually believed that the application of Kundt's rule is obscured by the formation of compounds between the dissolved compound and the solvent. The formation of such solvates seems to be quite definitely proven for some inorganic compounds and organic solvents.<sup>2</sup> Kauffman, Hantzsch and Glover, Gorke, Köppe and Staiger, and others, have recently shown that the extinction coefficient varies somewhat for every solvent. In the same solvent the extinction coefficient usually increases as radicals are added to the dissolved substance so as to increase its molecular weight. Hantzsch<sup>3</sup> gives evidence to show the presence of solvates and molecular aggregates in the case of nitrohydroquinone dimethyl ether.

An interesting investigation has been made by Kalandek.<sup>4</sup> Resonators will emit electromagnetic waves of different wave lengths, depending on the index of refraction of the liquid in which they are vibrating. Kalandek investigated the effect of different solvents on the period of various resonators and also on the positions of the absorption bands of a large number of organic compounds. In general, the relations were

<sup>1</sup> Physic. Rev., Dec., 1909; Feb., 1910.

<sup>2</sup> Anderson: Physic. Rev., **26**, 520 (1908). Jones and Strong: Physik. Z., **10**, 499 (1909); THIS JOURNAL, **43**, 37, 97 (1910).

<sup>3</sup> Ber. d. chem. Ges., **46**, 1556.

<sup>4</sup> Physik. Z., **9**, 128 (1908).

not very close. It would be very interesting, however, to carry these investigations into the infrared.

*The Absorption Spectra of Benzene and Its Derivatives.*—Benzene and several of its derivatives show selective absorption in the ultraviolet. Generally the absorption spectra of organic compounds consist of very wide diffuse bands. The absorption bands of gaseous benzene, on the other hand, are very fine. Benzene in solution shows seven absorption bands between  $\lambda$  2330 and  $\lambda$  2710, and in the gaseous state about 30 bands. Pauer,<sup>1</sup> Friedrichs,<sup>2</sup> Grebe<sup>3</sup> and Hartley<sup>4</sup> have investigated several of the benzene compounds. The bands in the gaseous state are much finer and usually more numerous than in solution or in the solid state.

Both the vapor and solution bands are shifted to the red when the radicals Cl, Br, CH<sub>3</sub>, etc., are substituted for hydrogen. The shift is generally greater the greater the molecular weight of the radical. The bands of benzene shifted in this way are the ones that are common to benzene, toluene, ethylbenzene and hydroxyxylene, and are unaffected by temperature and pressure. Hartley gives the following wave lengths for benzene:

	$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .
In sol'n	2682	2657-2642	2614-2600	2539	2480	2426.5	2376
As vapor	2670	2630	2590	2523	2466	2411	2360

As far as investigated, the substitution products of benzene have much less characteristic spectra than that of benzene itself. It would be very interesting to know whether the shift of the bands is gradual as the state is changed or as different chemical radicals are added.

Anthracene has the following bands:

	$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .	$\lambda$ .
Solid	4250	4495	4745	4980	5300
Solution	4050	4275	4540	4820	....
(Fluorescent) vapor	3900	4150	4320	....	....

The substitution of saturated groups in benzene has been found to change the absorption spectra but little. Unsaturated radicals like NH<sub>2</sub>, COOH, etc., change the spectra very greatly, so that there is hardly any relation to the benzene spectra. In the various di-substitution products, the para

<sup>1</sup> Wied. Ann., **61**, 363.

<sup>2</sup> Z. wiss. Phot., **3**, 154 (1905).

<sup>3</sup> *Ibid.*, **3**, 363 (1905).

<sup>4</sup> J. Chem. Soc., **77**, 839 (1900). Phil. Trans., **208**, A, 475-528 (1908).



compounds retain the characteristics of the benzene absorption better than the ortho or meta compounds. A considerable amount of work has been done by Hartley,<sup>1</sup> Baly and Desch,<sup>2</sup> Ley and von Engelhardt,<sup>3</sup> Baly and Collie,<sup>4</sup> Ley,<sup>5</sup> Hartley and Hedley,<sup>6</sup> Baly and Tuck,<sup>7</sup> and others, on the halogen, amino and nitro compounds of benzene, the phenols, pyridine, and its substitution products. Below are a few of the results established:

*Theory of Dynamic Isomerism.*—Baly, Stewart, Desch and others have recently supported the view that the absorption of light by organic compounds does not take place under ordinary conditions, but only when there is a change in the union of the atoms. In some cases this change of union takes place when a chemical compound changes into an isomeric form. Dynamic isomerism takes place when there is some third substance to act as a sort of go-between. Many substances are isodynamic only at high temperatures or in the presence of a catalytic agent. Sometimes the solvent may promote isomeric change. The point of equilibrium is determined by the velocities of the isomeric change, and these velocities are affected by the solvent, concentration, temperature, catalytic reagent, or the presence of free alkalis or acids.

An example of the above change is the transfer of a labile hydrogen atom from an oxygen or sulphur atom to a carbon or nitrogen atom. Sometimes an OH or CN group is transferred in the same way. The atom or radical transferred assumes a neutral condition compared with its condition as a powerful negative radical in the inorganic acids.

The theory of dynamic isomerism is useful in explaining a large number of phenomena in organic chemistry, and especially those connected with light emission and absorption. Tschugaeff<sup>8</sup> has examined some five hundred compounds for triboluminescence (luminescence due to the crushing of the compound) and has found that 25 per cent. of the organic compounds investigated showed a more or less intense flash when crushed. Most of the luminescent compounds could have existed in several isodynamic forms. Phosphorescence and fluorescence may be explained as being due to a dynamic

<sup>1</sup> Handbuch der Spectroscopie, Vol. III.

<sup>2</sup> J. Chem. Soc., **93**, 1345, 1747, 1902 (1908).

<sup>3</sup> Ber. d. chem. Ges., **41**, 2990.

<sup>4</sup> J. Chem. Soc., **87**, 1344.

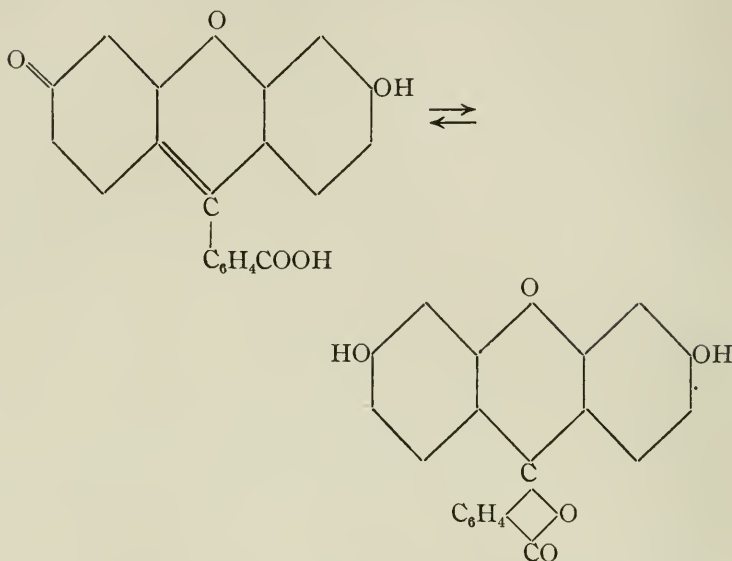
<sup>5</sup> Ber. d. chem. Ges., **41**, 1637.

<sup>6</sup> J. Chem. Soc., **91**, 319 (1907).

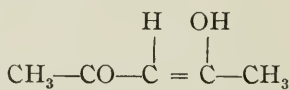
<sup>7</sup> *Ibid.*, **93**, 1902 (1908).

<sup>8</sup> Ber. d. chem. Ges., **34**, 1820 (1901).

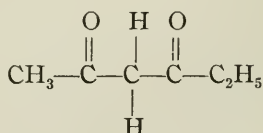
isomerism existing between two or more forms. For instance, fluorescein may exist in two or more forms:



We shall now consider some recent work by Baly and Desch. They first took up acetylacetone,  $\text{CH}_3\text{—CO—CH}_2\text{—CO—CH}_3$ , and ethyl acetacetate,  $\text{CH}_3\text{—CO—CH}_2\text{—CO}_2\text{C}_2\text{H}_5$ , and their metallic derivatives. Acetylacetone and its metal derivatives were found to give similar spectra. Ethyl acetacetate was found to give only a very slight general absorption, whereas its aluminium derivative gave a spectrum almost exactly like that of acetylacetone. Now the work of Perkin and others has shown that free acetylacetone is enolic and ethyl acetacetate ketonic.



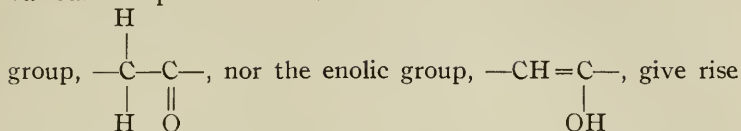
Acetylacetone (enolic).



Ethyl acetacetate (ketonic).

These results would then indicate that the metallic derivatives of ethyl acetacetate have the enolic structure, the metal taking the place of hydrogen in the OH group. But by using

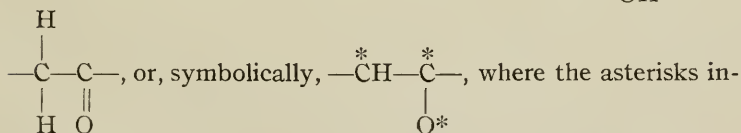
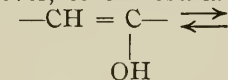
various compounds it was shown that neither the ketonic



to a trace of banded absorption. This would also result from Hartley's work.

It would seem probable, then, that the absorption was not to be attributed to any definite molecular structure but to a dynamic isomerism existing between the two modifications of the compound in solution. Now it was stated before that alkalis and acids change the velocity of the transformation from one form to the other, the final state being unaffected by the catalytic agent. This latter condition means that the direct and reverse actions are equally changed. If now intramolecular change is the source of the absorption bands, then a catalytic agent should affect the persistence of the band. Experimental results verified these conclusions. Other compounds were tried with similar results.

From these results it follows that there must exist, in connection with the reversible transformation of one tautomeric form into the other, a system which is synchronous with the light absorbed. This cannot be a vibration of the labile atom itself, for the oscillation frequency of the absorption bands does not bear any direct relation to the mass of the labile atom and the frequency of atomic motions is never so high as these. The absorption must be due, however, to the oscillation of linking of the keto-enol tautomers:



From a summary of work previously done on ultraviolet absorption spectra, it was seen that most of the compounds showing absorption also were tautomeric. As was also seen, an increase of the mass of the molecule in general decreased the oscillation frequency of the absorbed light, although by only a small amount.

Assuming the saturnian form of atom similar to the arrangement assumed by J. J. Thomson, chemical bonds would

simply consist of Faraday tubes of force. Now, by a rearrangement of Faraday tubes, it is quite probable that a vibrational disturbance would be set up. If Hewitt's explanation of the origin of fluorescence is correct, it would follow that disturbances set up by isodynamic changes are of the same frequency as light waves. The luminosity due to thermal or electric action is caused by rapid changes of stress or of the electric action to which the atoms are subjected. Here the disturbances of the electrons are due to the oscillation of linkages within the molecule. The comparatively small displacement of the absorption band by a change in the mass of the molecule is to be expected, for an increase of the mass of matter near a vibrating electron has the effect of retarding its motion, the oscillation frequency becoming less. For instance, the spectral series of Kayser for various related elements show a displacement towards the red on increasing the atomic mass. This is in general true for all emission spectra and for the absorption spectra of the rare earths and organic dyes.

The sodium and aluminium derivatives of ethyl acetate show the enolic and ketonic modifications in dynamical equilibrium. The sodium compound is found to be easily decomposed into sodium hydroxide and ethyl acetate, whereas the aluminium derivative shows dissociation and hydrolysis to but a very small extent. The absorption spectrum is not dependent on ionization or hydrolysis. Hartley has found that the ultraviolet absorption spectra of metallic nitrates is exhibited even on very great dilution, showing a close connection between the anion and cation in such solutions. Baly and Desch conclude that the Faraday tubes may be lengthened out on dilution and that the force necessary for the separation is furnished by the attraction of the solvent. Solvents which thus exert a strong attracting force are ionizing agents; and this attraction is exerted both on molecules and ions. We have thus hydrated molecules and ions. When the Faraday tubes are lengthened beyond a certain critical value, an interchange of ions between the molecules becomes possible. A completely dissociated solution of a salt is not one in which the ions are moving independently of one another, but one in which the length of the Faraday tubes is greater than the critical value. In tautomeric compounds the Faraday tubes connect the labile atom with the rest of the molecule, being lengthened out to such an extent as to allow these atoms to change their positions in the molecule, and there is a sort of internal ionization within the molecule. To this making and break-

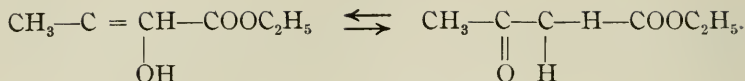
ing of Faraday tubes may be attributed the absorption of the light.

In the tautomeric aliphatic compounds the substitution of an alkyl group for the labile atom destroys the tautomerism. This would be expected, for alkyl ions are unknown. Water and other solvents do not have sufficient attractive force to lengthen out the Faraday tubes in this case. Whether there is a banded absorption in these cases is not stated. One consequence of the theory can be tested. Since the persistence of the absorption band is a measure of the number of molecules undergoing transformation at any moment, this persistence should reach a limit for each tautomeric compound when the length of the Faraday tubes has reached their critical length, so that free interchange takes place. By the successive addition of an accelerating compound a maximum should be found. Experiment shows this to be true. Take the case of ethyl benzoylsuccinate, to which 1, 10, 20, and 100 equivalents of sodium hydroxide have been added. The limits of persistence referred to a 0.0001 normal solution of the ester are as follows:

	Free ester. mm.	1 eq. NaOH. mm.	10 eq. NaOH. mm.	20 eq. NaOH. mm.	100 eq. NaOH. mm.
Absorption band begins at	120.0	63.0	40	31.7	21.9
Absorption band ends at	83.2	34.7	20	15.2	10.4
	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
Change of dilution over which the band persists	30.7	44.9	50	52.0	52.5

At this point it may be well to refer to the work of Stewart and Baly. Quite a number of chemical facts have been explained by the theory of steric hindrance, although this theory also fails to explain a great many things. For instance, acetic acid,  $\text{CH}_3\text{COOH}$ , is esterified with ease. The methyl, ethyl, etc., derivatives are much more difficult to esterify. This is explained as due to the larger volumes occupied by these radicals and the consequent hindrance to the approach of the alcohol to the carboxyl radical. If, as is probable, however, the intramolecular mean free path is large compared to the size of these radicals, this explanation by steric hindrance breaks down. The theory of isodynamic change will explain all these facts and also others where the theory of steric hindrance would lead to conclusions directly contrary to the facts. According to this theory acetacetic ester exists as



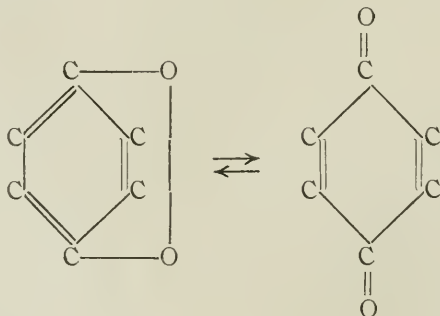


During this dynamic equilibrium there are periods during which a nascent carbonyl group exists. From analogy to the action of other nascent substances, this would occasion a very much greater reactivity.

Stewart and Baly, on further investigation, found that the absorption band in this case has a persistence which decreases proportionately to the decrease of reactivity of the ketone's carbonyl group. It has been noticed by chemists that the velocity of tautomeric change depends on the solvent. Stewart and Baly also found that the persistence of the absorption band was very different in aqueous and alcoholic solutions. In the case of pyruvic ester they show that the facts may be represented by the scheme



In tautomerism we have a wandering of the hydrogen atom, so Stewart and Baly propose to call this process Isorropesis (from the Greek word *ισορροπεία*, equipoise), or an oscillation in the carbonyl grouping. By the persistence of absorption bands it is possible to measure the activity of chemical compounds. The band produced by the isorropesis is also much nearer the red than that produced by the process of enol-keto tautomerism. An example of isorropesis would be the quinone band  $1/\lambda = 2480$ , which would be due to the following change:



In general, then, according to the theory of Baly, Desch, Stewart and Collie, any absorption by organic compounds is

due to the conditions that occur during isomeric changes. Benzene, for example, appears in two forms and the absorption spectrum is due to a condition of benzene while it is changing from one form to the other. This theory explains quite well the action of chromophores for, as we have seen, every chromophore contains at least one double bond.

*Theory of Stark.*—Stark<sup>1</sup> considers that chemical valency can be explained as due to the presence of negative electrons that hold the positive parts of atoms together. In Fig. I it is seen how this can take place, the dotted lines representing lines of electric force.

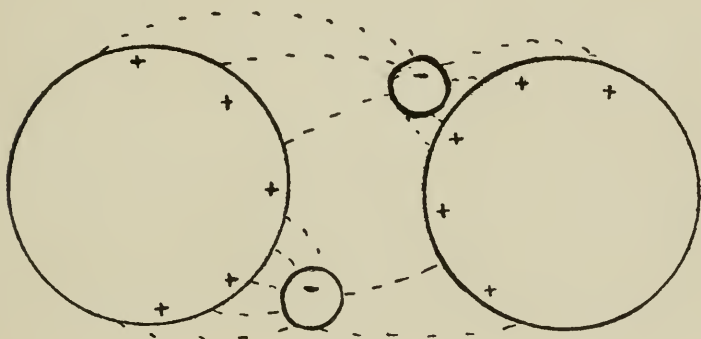


Fig. I.

The conditions represented in Fig. I are such that there is very little stray electric field beyond the atoms. Under such conditions the valency electrons are saturated and Stark represents this by the symbol  $\longleftrightarrow$ . Under many conditions, however, the valency electrons are not so closely united to the atoms and are more or less unsaturated. Under certain conditions an electron may be thrown off the atom and Stark considers that it is under some condition such as this that selective absorption of light takes place. When the electron returns to the atom it will undergo certain accelerations along its path and during these accelerations it will emit radiations. Stark believes that under some condition at least similar to this, the fluorescent radiation is emitted and that the period of this radiation will depend on the amount of energy set free when an electron recombines with the positive part of the molecule. From the heat changes which occur in various chemical reactions, Stark calculates what the approximate period of these radiations should be and in many

<sup>1</sup> Physik. Z., 9, 85 (1908).

cases obtains values which agree with the positions of known bands in the spectrum. Among these bands is the ultra-violet band of benzene. Stark's formula for benzene would be the following:

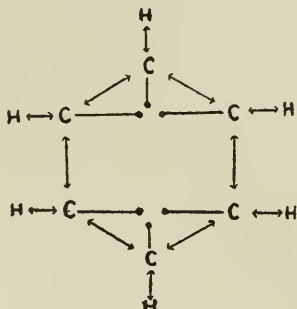
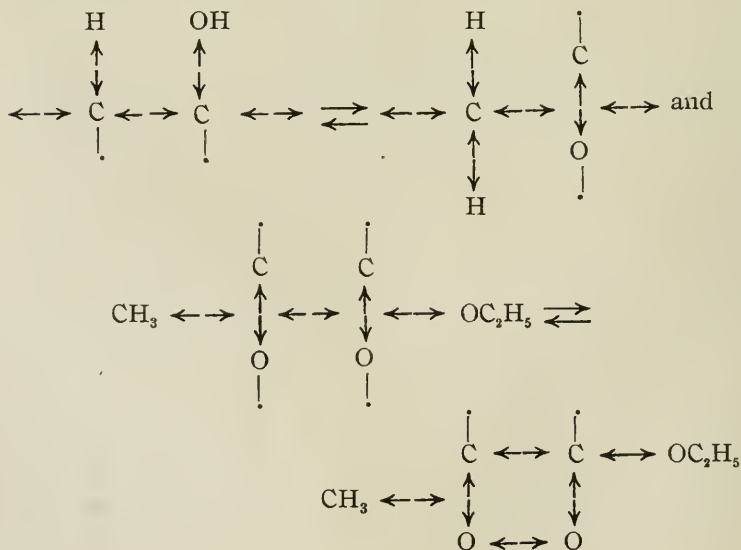


Fig II.

The symbol  $\text{—}\cdot$  simply means that one electron is not as closely joined as the other three to the carbon atom. It is possible that even this unsaturated electron may have lines of force running to the other carbon atoms. In this way partial valency can easily be explained. The keto-enolic and isorropesic changes, as interpreted according to Stark's theory, are represented as follows:



In this consideration of atoms it would be expected in general that the space containing the electric field of the electron would more or less envelop the positive nuclei of the atoms and that the volumes of atoms would depend on their valency. This would agree very well with the assumptions of Barlow and Pope.<sup>1</sup> These assumptions are as follows: In any chemical body the relative volumes of the atoms are proportional to their valencies; in a crystallized body the atoms are close packed; in a compound the volumes of the spheres of atomic influences of atoms of the same valency may differ slightly. The latter variation of the sizes of the spheres of influence (interpreted here as the space filled by the electric fields of the valency electrons) may be due to the different amounts of saturation, or, as Stark calls it, the lack of the valency electrons. It would be interesting to know whether the energy relations support this view, it being expected that the greater the lack of the electrons, the less the potential energy of the compound.

Stark and Steubing<sup>2</sup> have investigated the fluorescence of a large number of organic compounds. Most spectra are banded, and a band never runs in both directions. The band consists of a tail where the smaller bands are close together. From the tail the small bands may run towards the red or towards the ultraviolet, getting farther and farther apart all the time. But there are never small bands on both sides of the tail. The absorption of light by bands running "to the red" is not accompanied by fluorescence or by any photoelectric effects. The absorption of light in bands running towards the violet (benzene bands) is accompanied by a photoelectric effect, a fluorescence of the bands themselves and by a fluorescence of bands due to the connection of carbonyl, ethylene or other chromophoric groups if these be present in the molecule. The addition of more chromophores to the compound shoves the fluorescent bands to the red.

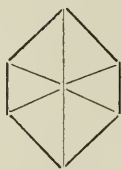
*Other Benzene Theories.*—There are some color changes of benzene compounds for which the general theory does not seem to account easily. For instance, nitronaphthalene is yellow. By introducing two nitro groups a colorless compound is obtained. In order to explain phenomena of this kind Kauffmann<sup>3</sup> assumes that the introduction of groups into a benzene nucleus may change the condition of the benzene

<sup>1</sup> J. Chem. Soc., **89**, 1675 (1906); **91**, 1150 (1907). Swartz: *THIS JOURNAL*, **37**, 638 (1907); **42**, 158 (1909).

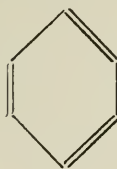
<sup>2</sup> Physik. Z., **9**, 481, 661 (1908).

<sup>3</sup> Z. physik. Chem., **50**, 530. Ber. d. chem. Ges., **37**, 2941.

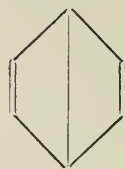
ring itself. He considers that benzene may have the diagonal, the Kekulé, or the Dewar<sup>1</sup> formula.



I.



II.



III.

In condition I benzene has an aliphatic character, as in nitrobenzoic acid,  $\text{C}_6\text{H}_4(\text{NO}_2)\text{COOH}$ . In this condition, having no double bonds, it does not possess strong color properties. The second condition has an aromatic character and is exemplified in the phenols. Examples of the third condition are found in aniline, *p*-phenylenediamine, naphthalene or anthracene. Of the three conditions, the second one is the best chromophore. According to Kauffmann, benzene vapor exists in the diagonal condition and for that reason it is not luminous when exposed to electric discharges of high frequency or to the rays from radium. Auxochromes and chromophores cause the benzene to become luminous and for this and other reasons Kauffmann thinks that the condition of the benzene grouping has been changed.

The different changes in color may be due to one or more of three conditions:

1. There may be no intramolecular changes of constitution, but the whole change of color may be due to the change in the radicals.

2. There may be an intramolecular rearrangement.

3. There may be an association of the molecules or compounds formed with the solvent. The above classification includes color changes that are not explained by isomerism.

In many cases it is practically impossible to decide between the different possibilities. Auwers<sup>2</sup> and Tuck<sup>3</sup> give evidence to show that the sodium salt of hydroxyazobenzene owes its color simply to the introduction of the sodium. Baly and Schaefer,<sup>4</sup> Hantzsch,<sup>5</sup> Vey, Gorke,<sup>6</sup> and others, give some cases coming under class 2. As example, we may take dinitroethane:

<sup>1</sup> Ber. d. chem. Ges., **33**, 1725; **34**, 682; **35**, 3668. Z. physik. Chem., **55**, 547.

<sup>2</sup> Ann. Chem. (Liebig), **360**, 11.

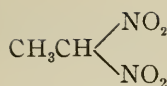
<sup>3</sup> J. Chem. Soc., **91**, 454 (1907).

<sup>4</sup> *Ibid.*, **93**, 1806.

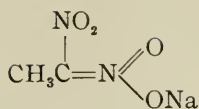
<sup>5</sup> Hantzsch: Ber. d. chem. Ges., **32**, 575. Hantzsch and Veit: *Ibid.*, **33**, 626. Ley and Hantzsch: *Ibid.*, **39**, 3149.

<sup>6</sup> Hantzsch and Gorke: *Ibid.*, **39**, 1073.

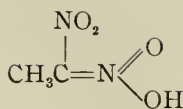




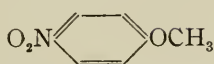
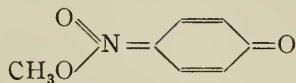
Pseudo acid, colorless.



Sodium salt, yellow.



Acid, yellow.

Nitrophenol ether, faintly yellow.  
Benzene derivative.Chromonitrophenol ether, deep  
red. Quinone derivative.

A very full discussion of the "Umlagerung" theory is given by Ley.<sup>1</sup> A short discussion is also given of the theory of indicators, of polymerization, and of metallic derivatives of organic compounds, especially of cases where the metal is supposed to be present in the inner part of the molecular complex.

W. W. STRONG.

## REVIEWS.

COLLOIDS AND THE ULTRAMICROSCOPE. A Manual of Colloid Chemistry and Ultramicroscopy. By DR. RICHARD ZSIGMONDY, Professor of Inorganic Chemistry in the University of Göttingen. Authorized Translation by JEROME ALEXANDER, M.Sc. With Two Colored Plates and Numerous Illustrations. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. xiii + 245.

An interesting treatment of the modern theory of colloidal solutions and suspensions, their physical and chemical properties, and the use of the ultramicroscope in their study. The ultramicroscope as developed by Siedentopf and Zsigmondy is merely the old device of oblique illumination pushed to the extreme limit. The powerful beam of light, traversing the fluid in a horizontal direction, is diffracted or scattered by the minute particles, and this light, entering the microscope, makes the particles visible as minute specks of light on a black background. A very complete exposition of this method for studying the movement (Brownian), size and distribution of the particles in suspension is given. Five chapters are devoted to colloidal gold alone, and there is much valuable information regarding the nature of jellies and gelatinous substances, hydrosols, colloidal sulphides, etc.

The book makes interesting reading for the chemist and physical chemist, although it is not as well arranged as it might be, and there are some repetitions. The pros and cons for and against various theories, by various writers and ex-

<sup>1</sup> Jahrb. d. Rad. u. Elek., 6, 341, 381 (1909).

perimenters, are so well mixed together that the reader is often in doubt about which to accept.

R. W. W.

THE MODERN ASPHALT PAVEMENT. By CLIFFORD RICHARDSON, M. Am. Soc. C. E. Second Edition. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1908. pp. ix + 629.

A more comprehensive and valuable work on this subject is hard to find. The author is of ripe experience and deeply rounded in his subject and has established successfully a reputation as an expert chemical engineer. The natural tendency, so frequently manifested by technical writers, to indulge too freely, for the convenience of the average reader, in professional language has apparently been carefully avoided and the book, without being unnecessarily verbose, is clear to the layman and to the professional. In matters of professional judgment, there always will be differences of opinion between experts, but the clear and positive expression of the judgment of one will always be of value to the others, whether or not they wholly agree. Both the statements of facts and of opinions in this work are clear and positive and generally as concise as proper consideration for the wide class of readers for which the book is intended will allow.

The subject is treated exhaustively. Very little of value seems to have been omitted and the book seems as nearly up to date as it is possible to expect, especially in view of the almost daily changes and discoveries being made in the subject under discussion.

The work is admirably arranged as to sequence of topics and an appreciable convenience is the "Summary" printed after each chapter, which gives briefly a description or the conclusions of the discussion of the chapter. The book is, in the judgment of the reviewer, well suited for use as a textbook in an engineering course and most valuable for reference to any one connected with the work it covers.

In accepting the statements of opinion or judgment made by the author, it, of course, should be remembered that the latter has been for many years, and we understand still is, employed by a concern deeply interested in the use of asphalt from a particular source. The impressions he has received through the media of his surroundings may, therefore, have been somewhat tinged in passing through the same, and it is possible that this explains some differences of opinion or judgment that, in spite of the undoubted effort of the author to be fair and impartial, exist between himself and others who have been differently situated. The book in its appearance reflects great credit on its publishers.

W. B. C.

PHYSICAL CHEMISTRY FOR ELECTRICAL ENGINEERS. By J. LIVINGSTON R. MORGAN, PH.D., Professor of Physical Chemistry in Columbia University. Second edition, revised. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. x + 249. Price, \$1.50.

The object of this work is to give "a knowledge of physical chemistry sufficient in scope for the understanding of current work in electro-chemistry." The book is divided into eight chapters, which treat respectively of atomic and molecular weights, of the properties of gases, the first and second laws of thermodynamics, solutions, chemical mechanics, equilibrium in electrolytes and electrochemistry. The final chapter consists of a set of problems with answers. The subject is placed on an experimental basis by discarding all hypothesis and by keeping before the reader's mind the experimental facts on which his ideas are based. The general method of treatment is clear and calls for no further special comment. One or two points that might be improved on may be mentioned. It is stated on p. 126 that to integrate the van't Hoff equation  $q$  must be considered independent of the temperature. This is not correct, as it may be integrated if  $q$  is a known function of the temperature.

The discussion of the decomposition of water is rather out of date, as it is now known that if the potential of oxygen could be measured it would be 1.22 volts against hydrogen, and that whatever the value 1.07 may mean, it is not the potential of the hydrogen-oxygen cell.

The problems cover all the matter contained in the text and are a valuable addition to the book. It is unfortunate, however, that more attention has not been paid to the proper use of insignificant figures, as for example in problem 56, where the data are given to two places and the answer is worked out to five.

These points, however, do not materially alter the value of the book to the beginner, to whom it may be safely recommended.

M. DEKAY THOMPSON.

A TEXT-BOOK OF PHYSICAL CHEMISTRY THEORY AND PRACTICE. By ARTHUR W. EWELL, PH.D., Asst. Professor of Physics, Worcester Polytechnic Institute. Philadelphia: P. Blakiston's Son & Co. 1909. pp. vii + 370. Price, \$2.25.

This book is a new departure as a text-book of physical chemistry, being "intended to serve as a laboratory manual, as a text-book to accompany recitations or lectures, and as a convenient book of reference," all in one. It bears very plainly the stamp of a teacher of physics. The usual aim of a course in physical chemistry is to equip prospective chemists with all the possible means of attacking their problems.

There are probably few teachers, therefore, who would consider it wise to follow this author and spend time on such things as the hygrometer, the measurement of the angle of a prism, of the velocity of sound and of the wave length of light, while giving but ten lines to colloidal solutions, two lines only of actual information about catalysis, nothing about mixed crystals, the real cause of hydrolysis, or association as indicated by surface tension.

There are several misleading statements. The modern "normal weight" of cane sugar does *not* produce the same rotation as 1 mm. of quartz, as stated on page 223. On page 272 we read of a "mixture (solid solution) of solid silver and solid eutectic alloy," a new definition of solid solution. The mercury still pictured on page 74 is antiquated since the work of Hulett.

The publishers' and proof-readers' work has been well done, though it is surprising to see a cut inverted on page 93. The text is clear, concise and well arranged. The experiments are interesting and suggestive, as the author has not given the usual miniature Ostwald-Luther. Since most teachers doubtless prefer to arrange their own course, the physical standpoint will not prevent the book from being a useful addition to their libraries.

JOEL H. HILDEBRAND.

PHYSIKALISCH-CHEMISCHE RECHENAUFGABEN. Von DR. R. ABEGG, Professor, und DR. O. SACKUR, Privatdozent, an der Universität Breslau. Leipzig: G. J. Göschen'sche Verlagshandlung. 1909. pp. 104. M. 0.80.

As the title implies, the booklet is a series of values and equations that are frequently used in physical-chemical calculations.

H. C. J.

CHEMICAL CONVERSION TABLES, for Use in the Analysis of Fertilizers, Fertilizing Materials, Iron and Its Products, Etc., Etc. By H. B. BATTLE, PH.D., and W. J. GASCOYNE, PH.D., Baltimore: Williams & Wilkins Pub. Co. 1909. pp. 79. Price, \$2.50.

Tables are given for phosphoric acid, potash, ammonia and protein, nitrogen, chlorine, sulphur, alumina, phosphorus and magnesia, silica, and manganese. The weight of precipitate obtained from 1 or 0.5 gram of sample is given to 0.1 milligram and the corresponding percentage of the substance sought to 0.01 per cent. The tables are clear and conveniently arranged. The book is designed for use in commercial laboratories and will prove a great time-saver for those who handle many analyses involving these substances. It is durably and elegantly bound in leather.

E. EMMET REID.

ELEMENTARY CHEMISTRY. By HOLLIS GODFREY, Head of the Department of Science, Girls' High School of Practical Arts, Boston, Mass. New York, London, Bombay and Calcutta: Longmans, Green & Co. 1909. pp. xiv + 456.

In contents this book, apparently intended for schools, differs from the average first-year college manual only in the omission of some of the rarer elements and compounds. The dissociation theory is introduced, technical processes are well described and illustrated, and the book requires as much work and intelligence on the student's part as most college books.

It differs from other books in its profuse illustrations and in the author's style. The illustrations are technically very fine and include apparatus, technical processes and portraits, while some of the pictures may be considered as art for art's sake. For example, a picture of a very fine ripe apple illustrates the statement underneath: "Unripe fruit is acid; the ripened fruit sweet because of the addition of sugar." An artistic picture of high waves at sea illustrates the fact that there is salt in sea water. As to the author's style a single quotation must suffice, for his rhetorical periods are lengthy. Bear in mind that this book is not a primer but is full of chemical fact calling for close study but adorned every few pages with a flight like the following on Avogadro's hypothesis:

"It was about a century ago that the Italian scientist, Avogadro, proposed this wonderfully simple yet daring theory. Briefly stated, it is as follows: 'The same number of molecules may be found in equal volumes of all gases which have the same temperature and pressure.' Think of two old deserted barns of exactly the same size, which stand on either side of some old country road. Suppose both barns are filled with barn swallows, with swallows sweeping to the eaves across the hay, by the old stalls, and through the harness room. Each barn would be filled with ever-moving life whose sum would be the sum of all the swallows in the barn. Change from the two barns full of swallows to two jars full of gases. A liter of chlorine gas standing beside a liter of hydrogen gas is in our belief filled with moving life. The molecules which constitute the matter of the gas are in constant motion, bounding and vibrating to and fro within the confines of the vapor. There are so many in even a liter of gas that our finite minds can scarcely imagine their number. Think, then, what a wonderful imagination a man must have had to conceive that every liter or other fixed volume of a gas contains exactly the same number of these tiny bodies."

This simile, as stated, may illustrate the kinetic theory



of gases; it does not illustrate Avogadro's law, unless swallows obey the gas laws which the author does not state in his description of the barns.

The author is not only sometimes vague in his rhetoric but is inaccurate in some statements. On page 154, in speaking of the Birkeland-Eyde process, he says: "The rushing air meets the terrific temperature of the electric flame, and a portion of its nitrogen is combined with the accompanying oxygen with production of various oxides of nitrogen, particularly nitrogen pentoxide." As a matter of fact, the only oxide of nitrogen stable enough to exist even momentarily under the working conditions is nitric oxide, and the work of completely transforming the nitric oxide to nitrogen dioxide and thence to nitric acid is carried on in the acid towers. On page 252, in speaking of Moissan's diamonds, the author says: "The jewels found were small and of various colors; only a few were white, so the cost of the process was much more than the value of the thing obtained." This gives a misleading impression. The author should have stated the crude fact that the largest of Moissan's diamonds was 0.5 mm. in diameter, and the total output commercially valueless.

It is an ungracious duty to review a conscientiously written book unfavorably, and it must be borne in mind that the book may impress others quite differently. It must be granted that if it is really true, as the author evidently believes, that long rhetorical introductions and similes help and do not repel intelligent girls in studying chemistry, and that this sugar-coating induces them to assimilate chemical theory and fact, then this is an exceptionally good text-book. E. R.

AN ELEMENTARY TREATISE ON QUALITATIVE CHEMICAL ANALYSIS. By J. F. SELLERS, Professor of Chemistry in Mercer University, Macon, Ga. Second Revised Edition, with Notes and Tables. Ginn & Co. 1909. pp. 176. Price, \$1.00.

The distinctive features in this book are the chapters on the theory of analytical operations admirably written from the standpoint of electrolytic dissociation, and the chapter on analytic separations with theory and examples for practice. The author simply and clearly emphasizes by questions, answers and examples the application of the dissociation theory. The methods of separation used are good. E. R.

# AMERICAN CHEMICAL JOURNAL

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[Contributions from the Sheffield Laboratory of Yale University.]

## CLXXXI.—ALKYLATION OF AROMATIC AMINO ACIDS: AMINOMETHYLBENZOIC ACIDS.

[THIRD PAPER.]

BY HENRY L. WHEELER AND CHARLES HOFFMAN.

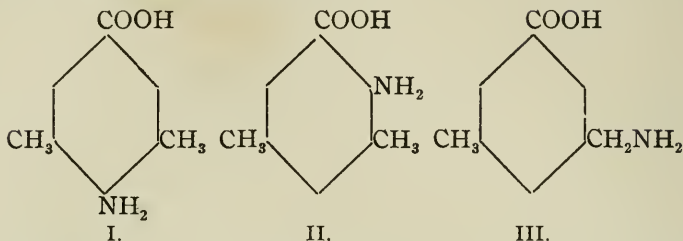
A review of the literature on the alkylation of aminobenzoic acids by means of alkali and alkyl halides was given in a recent article.<sup>1</sup> It was shown that while *o*-, *m*-, and *p*-aminobenzoic acids give N-alkylamino acids, certain substituted aminobenzoic acids, on the other hand, give esters. The amino acids having negative groups adjacent to the amino radical, as, for example, 3,5-diiod-*o*-aminobenzoic acid, 3,5-diiod-*p*-aminobenzoic acid, 3,5-dinitro-*p*-aminobenzoic acid, and 3-nitro-*o*-aminobenzoic acid, give esters; while 4-nitro-*o*-aminobenzoic acid, isomeric with the latter acid, but not having substituents in both of the adjacent positions to the amino group, gives N-alkyl derivatives.

With these results at hand, it was of interest to determine whether or not a similar protecting influence from substitution in the amino group is exerted by substituents which are not generally considered as having a negative character—the methyl group, for example. This also has the smallest molecular weight.

For this purpose the following aminomesitylenic acids were

<sup>1</sup> THIS JOURNAL, 43, 398 (1910).

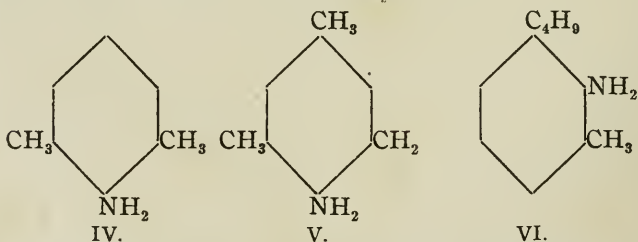
selected: 3,5-dimethyl-*p*-aminobenzoic acid (I) and 3,5-dimethyl-*o*-aminobenzoic acid (II).<sup>1</sup>



It must be remembered that in the alkylations we are dealing with the potassium salts of the acids in alcoholic solution and not the free acids. The alkali neutralizes the negative effect of the carboxyl group and therefore increases the positive character of the molecule.

It is interesting, in this connection, therefore, to note the behavior of similar amines. Friedlander<sup>2</sup> has shown that vicinal *m*-xylidine (IV) gives N-mono- and dialkyl derivatives with alkali and alkyl halides, less readily than aniline, while Fischer and Windaus<sup>3</sup> showed that this base does not give a quaternary ammonium iodide.

Mesidine (V) gives a secondary and a tertiary base but not a quaternary salt,<sup>4</sup> while Effront discovered that isobutyl-toluidine (VI) was not alkylated at all by potassium hydroxide and methyl iodide, even at 140°.<sup>5</sup>



<sup>1</sup> It is a noteworthy property of both the above amino-3,5-dimethylbenzoic acids that the hydrochlorides are hydrolyzed by water; when crystallized from water, the free acids are obtained and not the salts. This negative influence of the methyl groups was first observed in the case of 4-amino-3,5-dimethylbenzoic acid by Pittig and Brückner (Ann. Chem. (Liebig), **147**, 50).

<sup>2</sup> Monats. Chem., **19**, 644 (1898).

<sup>3</sup> Ber. d. chem. Ges., **33**, 345.

<sup>4</sup> Hofmann: Ber. d. chem. Ges., **5**, 718. Fischer and Windaus: *Loc. cit.*

<sup>5</sup> Ber. d. chem. Ges., **17**, 2346.

We have found that when 3,5-dimethyl-4-aminobenzoic acid (I) was warmed in alcohol with four molecular proportions of potassium hydroxide and five of ethyl iodide the alkylation took place slowly and the only product obtained besides unaltered acid was a primary amino ester,



In this case two methyl groups in the ortho position prevent the alkylation of the amino group.

When the isomeric acid, 3,5-dimethyl-2-aminobenzoic acid, was treated with potassium hydroxide and ethyl iodide, under the same conditions, a striking difference in behavior was observed. The acid underwent alkylation easily in a short time and the product consisted almost entirely of the N-diethylamino acid (30)<sup>1</sup> and the monoethylamino acid (10). A small amount of the ester (1) and unaltered acid (5) was also obtained.

In view of the behavior of the isomeric acid this seems to be a very curious result. In this case a methyl and a —COOK group in the ortho positions do not prevent the alkylation of the amino group. In fact they favor it, although the —COOK group has a much greater molecular weight than methyl. Here the stereochemical interference that might be expected is not shown in the reaction.

This result would be best explained if this amino acid had the structure represented by formula (III), but the statements of Jacobsen that with nitrous acid the acid gives oxymesitylenic acid and then 1,3,4-metaxyleneol,<sup>2</sup> and the observations of Schmitz,<sup>3</sup> who obtained the corresponding *m*-xylidine, are against this view. We have found that the ester of the nitro acid, from which the amino acid was prepared, does not have the properties of a compound containing the group —CH<sub>2</sub>NO<sub>2</sub>. It is insoluble in alkali. Formula (III) is therefore excluded.

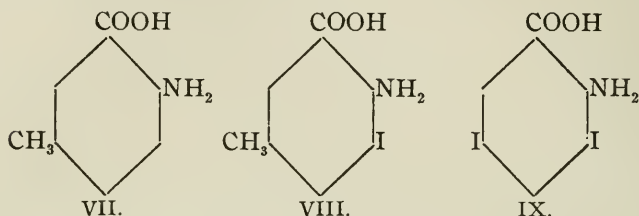
We have also examined the behavior on alkylation of methyl-anthranilic acid, 2-amino-5-methylbenzoic acid (VII), and

<sup>1</sup> The numbers in parentheses represent the relative parts by weight of the substances obtained.

<sup>2</sup> Ber. d. chem. Ges., **11**, 2055 (1878).

<sup>3</sup> Ann. Chem. (Liebig), **193**, 160.

of 2-amino-3-iod-5-methylbenzoic acid (VIII). The structure of the latter acid has not been settled, but from the behavior of anthranilic acid on iodation<sup>1</sup> it undoubtedly contains the iodine in the 3 position.



2-Amino-5-methylbenzoic acid alkylated readily and in a normal manner under the above conditions, giving a N-monoethylamino acid (15 parts) as the chief product. There were formed some N-diethylamino acid (1 part) and a small amount of material insoluble in ammonia (2 parts). This was probably the ester  $\text{CH}_3\text{C}_6\text{H}_3(\text{NH}_2)\text{COOC}_2\text{H}_5$ .

2-Amino-3-iod-5-methylbenzoic acid, prepared by treating methylanthranilic acid with iodine monochloride, alkylates with difficulty. The chief product besides unaltered acid (30 parts) was found to be the primary amino ester



(15 parts). A small quantity of the N-diethylamino acid (4 parts) was also obtained.

A  $-\text{COOK}$  group and an iodine atom in the ortho position to an amino group therefore exert an interference on the alkylation of the amino group. This interference is more pronounced when iodine also occupies the para position to the amino group than when methyl is present in this position. 3,5-Diiod-2-aminobenzoic acid (IX) gives no N-alkyl derivative, and no addition to or an alkylation on the nitrogen was observed when the ester of this acid was dissolved in ethyl iodide and the solution allowed to stand.<sup>2</sup>

These results show that neither the theory of stereochemical interference nor the positive or negative character of the

<sup>1</sup> Wheeler and Johns: *THIS JOURNAL*, **43**, 398 (1910).

<sup>2</sup> *THIS JOURNAL*, **43**, 409 (1910).



substituents is sufficient to give an explanation of the different behavior of amino acids on alkylation, and that other influences are at work to determine the course of the reaction. This subject will receive further attention when more data are collected.

The aminomethylbenzoic acids were obtained by reducing the corresponding nitro acids. 2-Nitro-5-methylbenzoic acid was prepared by nitrating *m*-toluic acid. Jacobsen<sup>1</sup> stated that 2-nitro-3-methylbenzoic acid and 2-nitro-5-methylbenzoic acid are formed in this nitration, the former in much larger amount.

This statement is incorrect. Panaotovic<sup>2</sup> showed that the chief product of the nitration is 2-nitro-5-methylbenzoic acid, melting at 219°, and we have now found that the isomeric acid which also results in this reaction is 4-nitro-3-methylbenzoic acid, melting at 211°, and not 2-nitro-3-methylbenzoic acid. The latter acid has not yet been prepared. We have found that the material supposed by Jacobsen to be this acid, melting at 182°, is a mixture of the acids melting at 219° and 211°. This material and the amino product obtained by reduction should be stricken from the list of acids.

#### EXPERIMENTAL PART.

*3,5-Dimethylbenzoic acid (mesitylenic acid)* was prepared by oxidizing mesitylene with dilute nitric acid. This is Fitig's method,<sup>3</sup> but he does not give the yields. Our experience with the method was as follows: Fifty-three grams of mesitylene were warmed on the steam bath with about 190 cc. of concentrated nitric acid diluted with two volumes of water; after being warmed about 40 hours under a return condenser, the oil was completely converted into a colorless crystalline mass. The acid solution and the crystalline material were separately distilled in steam. On adding alkali to the distillates, concentrating and precipitating with hydrochloric acid, 22.5 grams of mesitylenic acid, melting at 165°–166°, were obtained.

<sup>1</sup> Ber. d. chem. Ges., **14**, 2353 (1881).

<sup>2</sup> J. prakt. Chem., [2] **33**, 63 (1886).

<sup>3</sup> Ann. Chem. (Liebig), **141**, 144 (1867)

The residue from the crystalline material that did not distil in steam was converted into barium salts and the first crop of crystals which separated was recrystallized from water. On decomposing the salt then with hydrochloric acid, 1.5 grams of 4-nitro-3,5-dimethylbenzoic acid, melting at  $212^{\circ}$ – $217^{\circ}$ , were obtained.

The first filtrate from the barium salts was acidified with hydrochloric acid; this gave 23 grams of a mixture of acids melting at  $270^{\circ}$ – $300^{\circ}$ . Uvitic acid melts at  $287^{\circ}$  and trimesic acid above  $300^{\circ}$ .

The filtrate from the recrystallized barium salts, on acidifying with hydrochloric acid, gave a mixture of 4-nitro-3,5-dimethylbenzoic acid and uvitic acid. This was reduced with ferrous sulphate and ammonia, and on filtering, concentrating and acidifying with hydrochloric acid 4 grams of uvitic acid, melting at  $274^{\circ}$ ,<sup>1</sup> were obtained. On making the solution alkaline with ammonia, then precipitating with acetic acid, we obtained 1.4 grams of 4-amino-3,5-dimethylbenzoic acid.

In the above experiment a considerable quantity of the mesitylene was converted into high melting acids. This suggests that if a weaker nitric acid, or a smaller amount of it, were employed, or if the mixture were not warmed so long, a better yield of mesitylenic acid would result.

*2- and 4-Nitro-3,5-dimethylbenzoic Acids.*—The mesitylenic acid obtained above was nitrated according to Bamberger's directions.<sup>2</sup> In regard to the yields of the two acids formed there is only the statement of Schmitz<sup>3</sup> that the  $\beta$  acid or 4-nitro-3,5-dimethylbenzoic acid results in relatively small amount.

We have obtained, by nitrating 22.5 grams of mesitylenic acid, 19.5 grams of 2-nitro-3,5-dimethylbenzoic acid and less than one gram of the 4-nitro acid. In one experiment 20 grams of mesitylenic acid gave 25 grams of the mixed nitro acids.

The acids (23 grams) were separated as follows: The mix-

<sup>1</sup> Fittig and Furtenbach: *Ann. Chem. (Liebig)*, **147**, 295.

<sup>2</sup> *Ber. d. chem. Ges.*, **34**, 27 (1901).

<sup>3</sup> *Ann. Chem. (Liebig)*, **193**, 168 (1878).

ture was converted into the barium salts and the more difficultly soluble portion containing the 4-nitro-3,5-dimethylbenzoic acid was removed. On acidifying the filtrate the 2-nitro acid separated (19.5 grams).

The product precipitated (3.5 grams) from the barium salts that were removed melted at  $174^{\circ}$ – $176^{\circ}$ ; this agrees with the melting point of 4-nitro-3,5-dimethylbenzoic acid given by Schmitz. On crystallizing the sample once from alcohol the melting point rose to  $190^{\circ}$ – $217^{\circ}$ . The mixture was reduced, and in one experiment, on crystallizing the resulting amino acids, the two isomers were obtained, one melting at  $190^{\circ}$ , the other at  $242^{\circ}$ ; in the present case the amino acids (2 grams) were alkylated as described below, but only 0.24 gram of 4-amino-3,5-dimethylbenzoic acid was obtained, along with a small amount of the ester.

When the sample of 4-nitromesitylenic acid, obtained by oxidizing mesitylene with nitric acid, and melting at  $212^{\circ}$ – $217^{\circ}$ , was recrystallized from water it melted at  $215^{\circ}$ – $218^{\circ}$ . There was therefore no such lowering of melting point on crystallizing from water as described by Jacobsen.<sup>1</sup> In this respect our observation agrees with that of Emerson<sup>2</sup> on this acid.

*2- and 4-Amino-3,5-dimethylbenzoic Acids.*—The nitro acids were reduced with ferrous sulphate and ammonia, ten molecular proportions of the crystallized iron salt and 2 cc. of concentrated ammonia per gram of acid being used. This method of reduction gave a much better yield than tin and hydrochloric acid. One and a half grams of 4-nitro-3,5-dimethylbenzoic acid gave 1.1 grams of the amino acid; and 19.5 grams of the 2-nitro acid gave 14 grams of 2-amino-3,5-dimethylbenzoic acid.

From 53 grams of mesitylene we obtained 14 grams of 2-amino-3,5-dimethylbenzoic acid melting at  $190^{\circ}$ , and 2.74 grams of 4-amino-3,5-dimethylbenzoic acid, melting at  $242^{\circ}$ . Fittig<sup>3</sup> gives  $235^{\circ}$  and Emerson<sup>4</sup>  $245^{\circ}$ .

<sup>1</sup> Ber. d. chem. Ges., **11**, 2054.

<sup>2</sup> THIS JOURNAL, **8**, 269 (1886).

<sup>3</sup> Ann. Chem. (Liebig), **147**, 50.

<sup>4</sup> Loc. cit.

*Method of Alkylation and Separation of the Products.*—The alkylations described in this paper were carried out as nearly as possible in the same manner. The amino acids were dissolved in absolute alcohol containing four molecular proportions of potassium hydroxide, and five molecular proportions of ethyl iodide were added. The solutions were heated on the steam bath for 2–6 hours. If they developed an acid reaction the heating was stopped. The alcohol was then evaporated and the dry residue was treated with a little water. This dissolved any unaltered potassium salt, and since the acids are very difficultly soluble in cold water they could be precipitated by means of acetic acid. This gave an idea of the completeness of the reaction. The material left undissolved by water was then treated with cold, dilute ammonia, three parts of water to one of concentrated ammonia; after this treatment the residue, in each case, consisted of the primary amino ester. On adding acetic acid to the filtered ammonia solution any unaltered acid set free in the reaction was recovered. The N-alkyl acids, being soluble in water, were obtained on evaporating the solutions, acidified with acetic acid, to dryness and extracting the residues with organic solvents, ethyl acetate, etc. The N-dialkyl acids were separated from the other acids in this extract by taking advantage of their solubility in petroleum ether.

*Ethyl 3,5-Dimethyl-4-aminobenzoic Acid.*

*Ethyl 3,5-Dimethyl-4-aminobenzoate.*—One and two-tenths grams of the 4-amino acid and ethyl iodide and potassium hydroxide, in the proportions stated above, were heated in 30 cc. of absolute alcohol for five hours on the steam bath in a flask attached to a return condenser. The alcohol was then evaporated and the residue treated with water. From the aqueous solution acetic acid precipitated 0.75 gram, or 62 per cent. of the original amount, of unaltered acid, melting at  $242^{\circ}$ . When mixed with a sample of the original acid the melting point was not lowered. The reaction therefore was not complete.

The residue was treated with dilute ammonia; it did not

dissolve, and, on drying, weighed 0.6 gram, or 42 per cent. of the calculated.

This ester is readily soluble in benzene and alcohol, difficultly soluble in hot water, and moderately soluble in petroleum ether, from which it crystallizes in beautiful, colorless plates, melting to a clear oil at 67°.

N	Calculated for	Found.
	<del>C<sub>12</sub>H<sub>15</sub>N</del>	
	7.25	7.28

*see errata*  
*p. 596.*

When this substance was boiled with potassium hydroxide and the solution was acidified with acetic acid, 4-amino-3,5-dimethylbenzoic acid, melting at 242°, was obtained.

The above alkylation was repeated with two molecular proportions of potassium hydroxide and six of ethyl iodide and the mixture was digested on the steam bath for five days. Instead of increasing the yield of ester, this treatment caused decomposition, the products being a tar containing iodine and a small amount of unaltered acid.

#### *Ethylation of 3,5-Dimethyl-2-aminobenzoic Acid.*

*3,5-Dimethyl-2-diethylaminobenzoic Acid.*—Six grams of the acid were treated as above for 4 hours. The residue, on evaporation, almost all dissolved in water; an oily substance remained which, after treating with dilute ammonia and drying over sulphuric acid, weighed 0.1 gram. The amount of this was too small for purification, but it was shown to be the primary amino ester by saponification with alkali and precipitation with acetic acid, the regenerated acid melting at 190° being obtained. The ammonia solution, on acidifying with acetic acid, gave 0.5 gram of unaltered acid, and on evaporation only a very small residue remained.

The aqueous solution above gave no precipitate with acetic acid. It was evaporated to dryness and repeatedly extracted with ethyl acetate. The ethyl acetate extract was then extracted with petroleum ether; a part, which proved to be the N-monoethyl acid, remained undissolved. From the petroleum ether solution clear, colorless, prismatic crystals, melting to an oil at 98°, separated. About three grams of this



material were obtained. The following analyses show that it is a diethyl derivative:

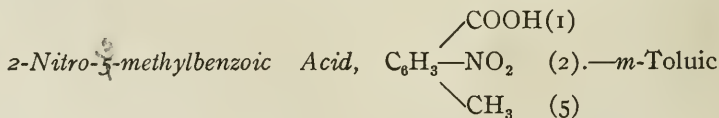
	Calculated for $C_{13}H_{19}O_2N$ .	I.	Found. II.
N	6.33	6.43	6.30

After boiling this material for 5 hours with alcoholic potassium hydroxide, evaporating to dryness with acetic acid and extracting the residue with petroleum ether the material was recovered unaltered. The substance is therefore a N-diethyl acid and not an ester. It is unaffected by boiling acetic anhydride, is readily soluble in water, ethyl acetate, benzene, chloroform, alcohol and acetone, and dissolves with difficulty in ether and petroleum ether. In the latter solvent it gives a beautiful, sky-blue fluorescence.

*3,5-Dimethyl-2-ethylaminobenzoic Acid.*—The residue remaining undissolved in petroleum ether was taken up in a small amount of hot water. Upon standing in a desiccator for some time, large, colorless prisms, melting at  $190^\circ$  with effervescence, separated. The first crop of these crystals weighed 1.0 gram. That we were not dealing with unaltered acid, which has the same melting point, was shown by mixing the substance with the original acid. The mixture melted at  $162^\circ$ .

	Calculated for $C_{11}H_{15}O_2N$ .	Found.
N	7.25	7.35

Alcoholic potassium hydroxide has no effect on the substance.



acid was nitrated according to Jacobsen's directions.<sup>1</sup> In one experiment 65 grams of the acid were added to 300 cc. of fuming nitric acid (sp. gr. 1.5). After pouring into water the product was converted into barium salts. The first crop of crystals that separated from water weighed 25 grams and the acid precipitated from this (18 grams) melted at about

<sup>1</sup> *Loc. cit.*

182°, the melting point given by Jacobsen for his so-called 2-nitrotoluic acid,<sup>1</sup> or  $\beta$ -nitro-*m*-toluic acid,  $\text{C}_6\text{H}_3\text{CH}_3\text{NO}_2\text{CO}_2\text{H}$ .

This was found to be a mixture, since on crystallizing only once from alcohol stout prisms, melting at 219°, were obtained. This material is 2-nitro-5-methylbenzoic acid. From the mother liquor, on standing, prisms, and finally fine needles, separated. On gently warming the solution the needles easily dissolved, leaving the prisms. The whole material was therefore crystallized from alcohol, and from the final mother liquor the needles were separated mechanically from the prisms. On crystallizing from alcohol they melted at 211°, the melting point of 3-methyl-4-nitrobenzoic acid. A portion was warmed with phosphorus pentachloride and poured upon ammonium carbonate. The amide obtained melted at 151°, crystallized in plates, and agreed in every respect with the amide of 3-methyl-4-nitrobenzoic acid prepared in a different manner by Beilstein and Kreuzler.<sup>2</sup>

2-Nitro-5-methylbenzamide, from the above acid melting at 219°, crystallized from alcohol in large, transparent prisms melting at 190°. It is moderately soluble in hot water and readily soluble in alcohol.

see errata  
p 596.

Calculated for  
~~C<sub>10</sub>H<sub>9</sub>NO<sub>2</sub>~~

Found.

N

15.3855

15.31

2-Amino-5-methylbenzoic Acid.—Jacobsen reduced the nitro acid melting at 219° with tin and hydrochloric acid. When we tried this method we found that the yield of amino acid was only about 25 per cent., the greater part of the material being converted into *p*-toluidine. By using ferrous sulphate and ammonia in the usual manner, the yield of amino acid was increased to over 90 per cent. of the calculated. This property of substituted nitrobenzoic acids of giving off the carboxyl group, when reduced with tin and hydrochloric acid, is a frequent cause of poor yields.

#### Ethylation of 2-Amino-5-methylbenzoic Acid.

2-Ethylamino-5-methylbenzoic Acid.—Four grams of the

<sup>1</sup> Beilstein: Handbuch, [3] 2, 1337.

<sup>2</sup> Ann. Chem. (Liebig), 144, 168.

above amino acid, melting at  $170^{\circ}$ – $171^{\circ}$ , were warmed in alcoholic solution with potassium hydroxide and ethyl iodide for six hours and then evaporated to dryness. After treating the residue with water and dilute ammonia it weighed 0.4 gram. This represented the amount of primary amino ester formed, since on saponification the unaltered acid was obtained.

On acidifying the aqueous solution, nothing separated. It was evaporated to dryness, the residue extracted with ethyl acetate, the ethyl acetate evaporated and the residue left extracted with ligroin. Large, transparent prisms, melting to an oil at  $71^{\circ}$ – $72^{\circ}$ , separated. The yield was about 3 grams.

	Calculated for $C_{17}H_{15}O_2N$ .	Found.
N	7.82	7.88

This acid is readily soluble in water, alcohol, benzene and chloroform, and difficultly soluble in ligroin, in which it shows a sky-blue fluorescence. It remained unaltered when boiled with alcoholic potassium hydroxide.

*2-Diethylamino-5-methylbenzoic Acid*.—Upon concentrating the ligroin solution by spontaneous evaporation a substance separated that was more soluble than the above monoethyl acid. It crystallized from ligroin in long, fine needles, melting to an oil at  $55^{\circ}$ – $57^{\circ}$ . When mixed with the monoethyl acid it melted at  $48^{\circ}$ – $50^{\circ}$ . The amount of this material obtained was about 0.2 gram and it was probably the N-diethyl derivative.

	Calculated for $C_{12}H_{17}O_2N$ .	Found.
N	7.13	7.23

From the ammonia solution 0.4 gram of unaltered acid was obtained.

*2-Amino-3-iod-5-methylbenzoic Acid*.—Three grams of iodine monochloride were added to a solution of 2.7 grams of 2-amino-5-methylbenzoic acid in a small amount of dilute hydrochloric acid and the mixture was warmed for an hour on the steam bath. A crystalline substance separated on warming; this was filtered, dissolved in ammonia, some sodium bisulphite

added, and then the solution acidified with acetic acid. The flesh-colored precipitate that separated weighed 3.8 grams, or 75 per cent. of the calculated. It was readily soluble in alcohol, difficultly in water, and moderately soluble in glacial acetic acid. It formed square plates from acetic acid and prisms from alcohol, which melted with decomposition at  $212^{\circ}$ .

	Calculated for $C_8H_8O_2NI$ .	I.	Found.	II.
N	5.06	5.15		5.05

*Ethylation of 2-Amino-3-iod-5-methylbenzoic Acid.*

*Ethyl 2-Amino-3-iod-5-methylbenzoate.*—The ethylation in this case was carried out in the usual manner with 4.8 grams of the above acid and the solution was warmed for two hours. The residue, on treating with water, left an oil which solidified in a freezing mixture. A portion dissolved when treated with dilute ammonia. The undissolved portion was dried over sulphuric acid; it weighed 1.5 grams. It was readily soluble in alcohol and petroleum ether; from the latter it formed long, colorless prisms, melting to an oil at  $70^{\circ}$ – $71^{\circ}$ .

	Calculated for $C_{10}H_{12}O_2NI$ .	Found.
N	4.60	4.76

On saponification it gave the unaltered acid.

Acetic acid precipitated 0.5 gram of unaltered acid from the aqueous extract.

*2-Diethylamino-3-iod-5-methylbenzoic Acid.*—When the ammonia solution was acidified with acetic acid 2.4 grams of unaltered acid were obtained. The solution was then evaporated to dryness, whereupon a small amount of sticky residue remained. This was extracted with petroleum ether and on concentrating the solution 0.4 gram of fine, hairlike crystals, which melted to an oil at  $125^{\circ}$ – $126^{\circ}$ , separated. This material was moderately soluble in petroleum ether and rather difficultly soluble in cold water.

	Calculated for $C_{12}H_{16}O_2NI$ .	Found.
N	4.20	4.10

Alcoholic potassium hydroxide had no effect on the substance.

NEW HAVEN, CONN.,  
May, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

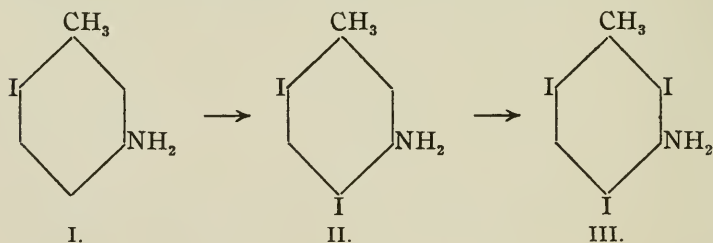
## CLXXXII.—ON THE ACTION OF IODINE ON META-TOLUIDINE.

BY HENRY L. WHEELER.

EXPERIMENTAL WORK BY CHARLES A. BRAUTLECHT, CHARLES HOFFMAN AND SAMUEL R. SCHOLES.

In previous papers<sup>1</sup> we have shown that when *p*-toluidine is mixed with iodine a mono- and a diiod derivative can easily be obtained, while under the same conditions *o*-toluidine yields a monoiod compound.

In the present paper we describe the compounds obtained by the action of iodine on *m*-toluidine. In this case the tendency of the base to take up iodine is most pronounced and at least the three following compounds are formed:



With the quantities of *m*-toluidine employed by us, no other iodine derivatives were isolated. It is probable that isomeric products are produced in small amounts in this reaction; some 4-iodo-*m*-toluidine and also 2,6-diiodo-*m*-toluidine might be expected. The 6 position is the first point of attack, as in the case of the action of bromine, nitric acid, etc.

6-Iodo-*m*-toluidine (I) has been obtained by Artmann<sup>2</sup> by an indirect method. The other derivatives are new. Their structure was determined as follows: 4-Iodo-*m*-toluidine<sup>3</sup>

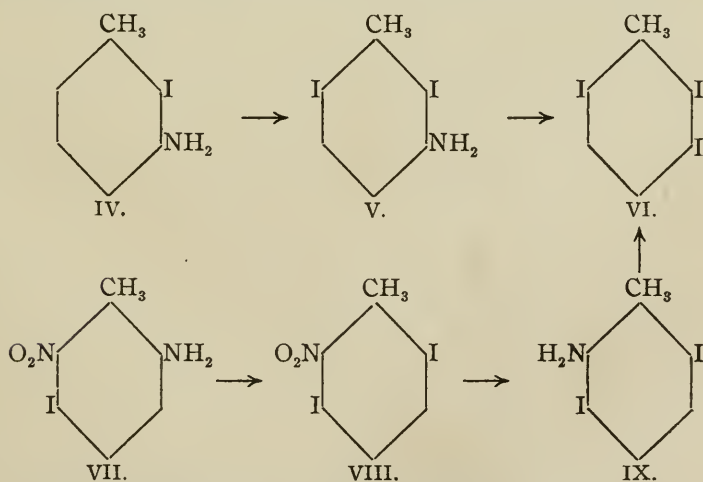
<sup>1</sup> Wheeler and Liddle: *THIS JOURNAL*, **42**, 441, 489 (1909).

<sup>2</sup> *Monats. Chem.*, **26**, 1099 (1905).

<sup>3</sup> From 3-nitro-4-iodotoluene. Willgerodt and Simonis: *Ber. d. chem. Ges.*, **39**, 269 (1906).



and 6-iod-*m*-toluidine, when mixed with iodine, gave the 4,6-diiod compound (II), while this compound and 2,6-diiod-*m*-toluidine gave the same triiod-*m*-toluidine (III). The new 2,6-diiod-*m*-toluidine (V below) was prepared from 2-iod-*m*-toluidine (IV)<sup>1</sup> by treating the acetyl compound of the latter base with iodine monochloride and then saponifying. That this procedure produced 2,6-diiod-*m*-toluidine was established by first preparing 2,3,6-triiodtoluene (VI) from this base, by diazotizing and replacing the amino group by iodine; and, then again, the same triiodtoluene, melting at 80°.5, was obtained from 2,6-dinitrotoluene. The latter process was carried out as follows: From the dinitrotoluene we prepared 6-nitro-*o*-toluidine by reducing with ammonium sulphide. When this base was treated with iodine it gave 5-iod-6-nitro-*o*-toluidine (VII) and then, on replacing the amino group with iodine, we obtained 2,5-diiod-6-nitrotoluene (VIII), or 2-nitro-3,6-diiodtoluene. This was reduced with ferrous sulphate and ammonia and the resulting 3,6-diiod-*o*-toluidine (IX) was converted into 2,3,6-triiodtoluene in the usual manner. The two methods of preparing this substance, which not only settle the structure of the triiodtoluene but also that of 2,6-diiod-*m*-toluidine, may be represented as follows:



<sup>1</sup> Wheeler and Liddle: *THIS JOURNAL*, **42**, 452 (1909).

## EXPERIMENTAL, PART.

*The Action of Iodine on m-Toluidine.*—When *m*-toluidine is mixed with iodine in molecular proportions (1 molecule base :  $I_2$ ) in the presence of ether, water and an excess of calcium carbonate, a mixture of unaltered toluidine and of mono- and diiodtoluidines is obtained.

The same is true when the base is treated with iodine in the proportion 1 molecule toluidine :  $I_3$ .

When the proportion of the reacting substances is 1 molecule base :  $I_4$ , the product consists of a mixture of mono-, di- and triiodtoluidines in which the amount of the di-derivative predominates, while one molecular proportion of the base and three of iodine ( $I_6$ ) give triiodtoluidine and resinous material. The greater the proportion of iodine used the more tar or resin is formed. Iodine determinations were made by Carius' method. If the substances were heated long enough and high enough (near  $300^\circ$ ), good results were usually obtained; otherwise the analytical figures were below the calculated.

All of the monoiod derivatives of *m*-toluidine have a disagreeable odor. In the case of 5-iod-*m*-toluidine, which is the only one that is stable on keeping, it is scarcely noticeable, while 4-iod-*m*-toluidine has the most pronounced odor.

A slight impurity decidedly lowers the melting point of these bases, and also that of the iodtoluenes, the lower iodine derivatives remaining liquid when impure. All of the compounds described in this paper liberate iodine when moistened with sulphuric acid and heated. Iodine in the aromatic group appears to be more sensitive towards acids than alkalies.

BY CHARLES HOFFMAN.

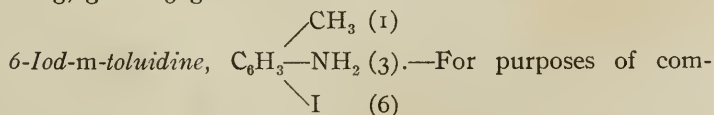
The following experiment illustrates our method of examining the reactions: Ten grams of *m*-toluidine were dissolved in 30 cc. of ether. The solution was placed in a large distilling flask and 35.6 grams of iodine (calculated for  $I_3$ ), 10 grams of calcium carbonate, and 30 cc. of water, were added. The mixture was heated on the steam bath until the iodine disappeared. The ether was then evaporated and the residue distilled with steam. The first two liters of

distillate contained an oil which did not solidify on cooling. The remaining portions of the distillate gave, on standing, crystalline material which weighed 15 grams and, on crystallizing from alcohol, melted at  $73^{\circ}$ – $74^{\circ}$  (4,6-diiod-*m*-toluidine). The oil from the first portions of the distillate was extracted with benzene and treated with acetic anhydride; this gave two acetyl derivatives: 3.5 grams of material melting at  $132^{\circ}$ – $134^{\circ}$  (6-iod-*m*-acettoluide), and about one gram of *m*-acettoluide. A black, resinous substance remained in the distilling flask. This was extracted with alcohol, but nothing was obtained. There was therefore no evidence of the formation of triiod-*m*-toluidine. In the above experiment about 8 per cent. of the *m*-toluidine remained unaltered, 14 per cent. was converted into 6-iod-*m*-toluidine and 45 per cent. into 4,6-diiod-*m*-toluidine.

When two molecular proportions of iodine were used ( $I_4$ ), 24 grams of *m*-toluidine, after 4 hours' heating, gave a little unaltered material, 2.5 grams of monoiodtoluidine, 30.5 grams of diiodtoluidine, 3 grams of triiodtoluidine and resinous material. Eight per cent. of the *m*-toluidine was changed to monoiod-, 38 per cent. to diiod-, and 3 per cent. to triiod-*m*-toluidine.

When three molecular proportions of iodine were used ( $I_6$ ), ten grams of the base, after 40 hours, gave no unaltered toluidine or mono- or diiodtoluidine on distilling with steam, but, on extracting the black residue with alcohol, 15 grams of triiodtoluidine were obtained, which corresponds to 35 per cent. of the *m*-toluidine employed.

The yields vary to a considerable extent with slight changes of conditions. In another experiment, for example (Brautlecht), 5 grams of *m*-toluidine, when treated with the calculated amount of iodine ( $I_6$ ) in three portions and not warmed as long, gave 13 grams of the triiod derivative.



parison this compound was prepared by Artmann's method.<sup>1</sup>

<sup>1</sup> *Loc. cit.*

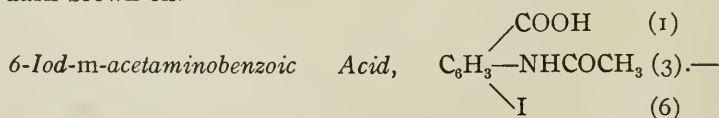
*o*-Acettoluide was nitrated<sup>1</sup> and the *5-nitro-o-toluidine* was converted into *2-iod-5-nitrotoluene*. This, on reduction, gave a base which, when purified by distilling in steam and crystallizing from petroleum ether, melted at 37°–39°. Artmann states that the iodtoluidine prepared in this manner melts at 98°–99° and the acetyl derivative at 132°. We have prepared the base by three different methods and in each case it melted at 37°–39° and the acetyl derivative at 132°–134°.

The best method for the preparation of *6-iod-m-toluidine* was found to be as follows: Twenty grams of *m*-acettoluide were dissolved in 20 cc. of glacial acetic acid and treated with 22 grams of iodine monochloride (one molecule) and this mixture was heated on a water bath, under a return condenser, for one hour. Upon adding water a dark substance separated, which lost most of its color on shaking with acid sodium sulphite. When crystallized from alcohol, 24.2 grams of *6-iod-m-acettoluide*, melting at 132°–134°, or 70 per cent. of the calculated amount, was obtained.

In order to obtain the free base from this acetyl compound, 14.2 grams of the latter were dissolved in a small amount of alcohol containing 8.7 grams of potassium hydroxide. After boiling for two hours the alcohol was evaporated and the residue distilled with steam. We obtained 8.85 grams of white crystalline material melting at 37°–39° (74 per cent. of the calculated), the melting point of which did not change when crystallized from petroleum ether.

*m*-Acettoluide was treated with two molecular proportions of iodine monochloride, but only the above monoiod derivative was obtained. Both *m*-acettoluide and the free base give the same monoiod derivative.

*6-Iod-m-toluidine* crystallizes from petroleum ether in colorless plates which have a disagreeable odor. They soon become brown on standing in the air and decompose, leaving a dark brown oil.



<sup>1</sup> Reverdin and Crépieux: Ber. d. chem. Ges., **33**, 2498.

Twenty-five grams of 6-iod-*m*-acettoluide were suspended in a liter of water and 24 grams of magnesium sulphate were added. This mixture was stirred by passing steam into it and a solution of 30 grams of potassium permanganate in a liter of water was slowly added. After heating 24 hours, the excess of permanganate was removed by adding alcohol. The solution was evaporated to a small volume, filtered and acidified with hydrochloric acid. This gave 14.4 grams of nearly pure acid, or 52 per cent. of the calculated. It was moderately soluble in hot water and crystallized in long, colorless, prismatic needles, which melted to a clear oil at  $210^{\circ}$ . It was readily soluble in alcohol and was not precipitated from alkaline solutions by acetic acid.

	Calculated for $C_9H_8O_3NI$ .	Found.
N	4.59	4.50

In view of the stability of isomeric iodaminobenzoic acids, namely 3-, 4-, or 5-iod-2-amino-, 5-iod-3-amino-, and 5-iod-4-aminobenzoic acids,<sup>1</sup> we were surprised to find that 6-iod-3-aminobenzoic acid from the above acetyl derivative is an extremely unstable substance.

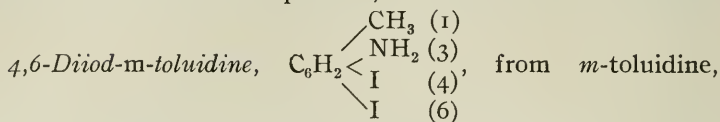
An attempt was made to saponify the acetyl compound with dilute hydrochloric acid. The solution was warmed for about a half hour and then cooled. Colorless needles, which formed burrlike crystals, separated. These were probably the hydrochloric acid salt. They were filtered off and dissolved in ammonia and the solution was acidified with acetic acid; no precipitate was formed, but a dark, inklike solution resulted, and on evaporation a coal-black residue was obtained. This dissolved in alkali, giving a black solution which, on acidifying with hydrochloric acid, turned deep blue and deposited an amorphous, flocculent, blue precipitate.

When the acetyl derivative was saponified by warming with alcoholic potassium hydroxide, the alcohol evaporated, and the aqueous solution acidified, the same result was obtained. It may also be stated that when iodine is added to an

<sup>1</sup> Wheeler and Liddle: *THIS JOURNAL*, **42**, 456, 499 (1909).



aqueous solution of the potassium salt of *m*-aminobenzoic acid and the solution evaporated, the same result is obtained.



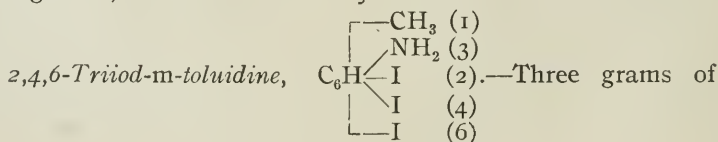
6-iod-*m*-toluidine, or 4-iod-*m*-toluidine (Scholes) and iodine, crystallizes from alcohol in large, thick, colorless needles or spikes, which turn brown when exposed to the air. It is readily soluble in alcohol, petroleum ether, ether and benzene, and melts to a clear oil at  $73^\circ\text{--}74^\circ$ . It forms, with hydrochloric and sulphuric acids, difficultly soluble salts, which are decomposed by water. The hydrochloride crystallizes in long needles from alcohol, but on boiling the solutions vapors of iodine are given off.

	Calculated for $\text{C}_7\text{H}_7\text{NI}_2$ .	Found.
N	3.90	3.93
I	70.75	70.93

The *acetyl derivative*,  $\text{C}_7\text{H}_5\text{I}_2\text{NHCCH}_3$ , is difficultly soluble in alcohol and almost insoluble in water. It forms long, fine, colorless needles melting at  $213^\circ$ .

	Calculated for $\text{C}_9\text{H}_9\text{ONI}_2$ .	Found.
N	3.49	3.60

The inertness of this acettoluide towards potassium permanganate is noteworthy. When 11 grams were warmed for seven days with a dilute solution of potassium permanganate and an equal weight of magnesium sulphate only 0.4 gram of material with acid properties, melting at  $260^\circ$ , was obtained. The remaining material was recovered unaltered. In another experiment the material was heated in a closed tube for 4 hours at  $200^\circ$  with a solution of potassium permanganate; even in this case only a small amount was oxidized.



4,6-diiod-*m*-toluidine were treated with one molecular proportion of iodine in the presence of ether, water, and an excess of calcium carbonate. After heating 8 hours the mixture was filtered and the residue extracted with alcohol. The yield of triiod-*m*-toluidine was 2.8 grams, or 70 per cent. of the calculated.

The material for analysis was prepared from *m*-toluidine and iodine (by Brautleucht) as described above.

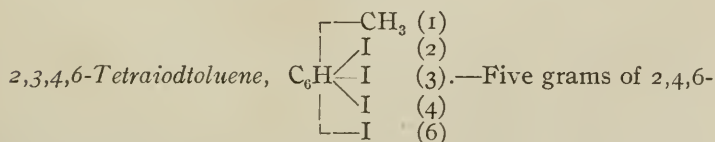
	Calculated for $C_7H_6NI_3$ .	Found.
N	2.89	2.91
I	78.56	78.29

This triiodtoluidine was also prepared by the action of iodine on 2,6-diiod-*m*-toluidine (Brautleucht, below). This settles the structure of the compound and that of the following derivatives:

2,4,6-Triiod-*m*-toluidine crystallizes from alcohol, in which it is quite difficultly soluble, in the form of long, pale brown, hairlike needles, which melt sharply to an oil at  $135^\circ$ . Further crystallization from alcohol did not alter the melting point or remove the color. It does not form salts with aqueous acids.

2,4,6-Triiod-*m*-acetotoluide,  $C_7H_4I_3NHCOCH_3$ .—When the above triiodtoluidine was warmed on the steam bath with acetic anhydride no reaction took place. Two grams of the base were warmed on the steam bath for 2 hours with an excess of acetyl chloride. This gave the acetyl compound. It is moderately soluble in alcohol and crystallizes in radiating clusters of needles, which melt to a dark oil at  $265^\circ$ .

	Calculated for $C_9H_8ONI_3$ .	Found.
N	2.66	2.83

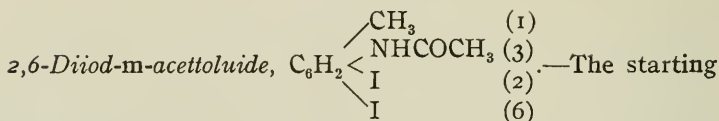


triiod-*m*-toluidine were dissolved in 15 cc. of concentrated sulphuric acid, cooled in a freezing mixture. To the deep

purple solution 1.8 grams of dry powdered sodium nitrite (2 molecules) were added. The mixture was then poured on finely crushed ice. This gave a light lemon-colored diazo solution which was filtered into a solution of 12 grams of potassium iodide in a small amount of ice water. The dark brown diazo iodide which separated was decomposed by warming the solution, and the product was treated with acid sodium sulphite. The material was then almost colorless and weighed 6 grams, or 92 per cent. of the calculated. It was difficultly soluble in alcohol and only moderately soluble in benzene. From the latter solvent it crystallized in long needles and melted to a clear oil at  $170^{\circ}$ .

	Calculated for $C_7H_4I_2$ .		Found.
I	85.23	<i>all errata</i> <i>p. 304</i>	<del>64.60</del> 84.60

BY CHARLES A. BRAUTLECHT.



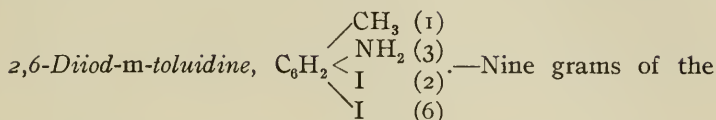
point for the preparation of this compound and the free base was *o*-acettoluide. This was nitrated according to the directions of Reverdin and Crépieux.<sup>1</sup> The 3-nitro-2-aminotoluene thus obtained was converted into 3-nitro-2-iodtoluene and this was reduced with ferrous sulphate and ammonia to 2-iod-m-toluidine,<sup>2</sup> melting at  $41^{\circ}$ – $42^{\circ}$ . The action of iodine on this base gave a mixture of products, while the acetyl compound and iodine monochloride reacted smoothly. The 2-iod-m-acettoluide (9.8 grams), melting at  $135^{\circ}$ , was dissolved in a small amount of glacial acetic acid. On adding iodine monochloride (11.6 grams) an immediate reaction took place and heat was evolved. The mixture was warmed for about 5 minutes on the steam bath and then allowed to stand for sixteen hours. Crystals separated, and when water was added to the glacial acetic acid solution more of the same material was obtained. It was difficultly soluble in alcohol and formed colorless prisms which melted to a clear oil at

<sup>1</sup> *Loc. cit.*

<sup>2</sup> Wheeler and Liddle: *THIS JOURNAL*, **42**, 452 (1909).

171°. The yield in two experiments was 78 per cent. of the calculated.

	Calculated for $C_6H_9ONI_2$ .	Found.
N	3.49	3.56

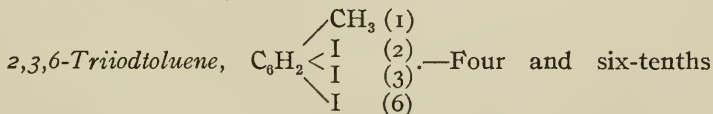


above acetyl derivative were saponified by boiling with 3.6 grams potassium hydroxide in alcoholic solution. At the end of two hours the product was distilled in steam, whereby the base slowly distilled over. The first portion of the distillate was oily, while the remainder gave colorless needles and prisms which were crystallized from alcohol and petroleum ether. The material then melted at 88°. The yield was 82 per cent. of the calculated.

	Calculated for $C_7H_7NI_2$ .	Found.
N	3.90	3.82

2,6-Diiod-*m*-toluidine gives a hydrochloride which is difficultly soluble in 10 per cent. hydrochloric acid and readily soluble in alcohol. It is decomposed by water.

When this base was treated with one molecular proportion of iodine in ether solution and then warmed on the steam bath the reaction was over in a short time. The product separated from ether in needles melting at 135° and when crystallized from alcohol or mixed with the triiod-*m*-toluidine above, the melting point was not altered. The latter compound is therefore 2,4,6-triiod-*m*-toluidine.



grams of 2,6-diiod-*m*-toluidine and 1.2 grams of dry sodium nitrite were mixed with 20 grams of concentrated sulphuric acid at 0°. This mixture, treated with crushed ice, formed a diazo solution, leaving only a small amount of undissolved material. This was filtered and added to a solution of 12.8

grams of potassium iodide in ice water. After warming, then treating with sodium bisulphite and cooling, the crystalline mass obtained amounted to 93 per cent. of the calculated. When crystallized from alcohol it was found to be difficultly soluble and formed colorless needles, which melted sharply to a clear oil at  $80^{\circ}$ .<sup>5</sup> It is practically nonvolatile in steam. Two and a half liters of distillate contained about 0.05 gram.

	Calculated for $C_7H_5I_3$ .	Found.
I	81.06	81.18

In regard to the structure of the above compounds, it is to be noticed from their method of preparation that iodine is known to be in the 2 and 3 positions. That iodine is also in the 6 position is proved by preparing this triiodtoluene from 2,6-dinitrotoluene.

6-Nitro-o-toluidine,  $C_6H_3$   $\begin{matrix} \diagup CH_3 (1) \\ \diagdown NH_2 (2) \\ \diagdown NO_2 (6) \end{matrix}$ .—This was prepared by reducing 2,6-dinitrotoluene (Kahlbaum) with ammonium sulphide.<sup>1</sup> As the yield was 96 per cent. of the calculated we give the details: Twenty grams of the dinitrotoluene was mixed with 60 cc. of 95 per cent. alcohol and 50 cc. of concentrated ammonia. Hydrogen sulphide was passed into the mixture for one hour and the solution gently warmed at first. The contents of the flask were transferred to a casserole and the alcohol evaporated. The residue was extracted with hydrochloric acid and precipitated with ammonia. The base melted at  $91^{\circ}$ .<sup>5</sup>

5-Iod-6-nitro-o-toluidine,  $C_6H_2$   $\begin{matrix} \diagup CH_3 (1) \\ \diagdown NH_2 (2) \\ \diagdown I (5) \\ \diagdown NO_2 (6) \end{matrix}$ .—Molecular propor-

tions of the above nitrotoluidine and iodine were warmed with ether, water and calcium carbonate for several hours. The ether was evaporated and the residue extracted with boiling alcohol and the material then precipitated from the alcoholic solution by adding dilute ammonia. The yields varied

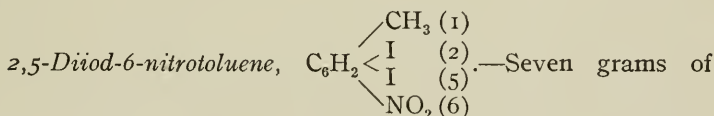
<sup>1</sup> Cunerth: Ann. Chem. (Liebig), **172**, 223 (1874). Ullmann: Ber. d. chem. Ges., **17**, 1959 (1884). Berntsen: *Ibid.*, **15**, 3018 (1882).



to a considerable extent; in one case in which we used 20 grams of base, the product was mostly tar or resinous material. When 5 grams or less were used the yields in eight experiments amounted to 70–87 per cent. This iodinitrotoluidine forms, from alcohol, beautiful yellow prisms, which melt sharply to a clear oil at 85°.

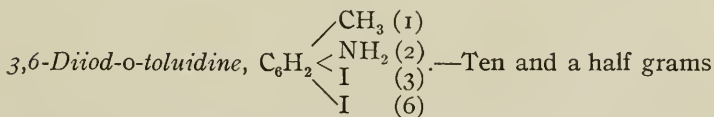
	Calculated for <del>C<sub>7</sub>H<sub>5</sub>O<sub>2</sub>NI<sub>2</sub></del>	Found.
N	10.07	10.04

The action of iodine monochloride on 6-nitro-*o*-toluidine in glacial acetic acid gave a dark brown tar as the chief product.



the above base were diazotized and treated with potassium iodide as in the case of 2,3,6-triiodtoluene. The yield was almost quantitative. The material is readily soluble in hot alcohol and forms colorless needles, which melt to a clear oil at 105°.

	Calculated for C <sub>7</sub> H <sub>5</sub> O <sub>2</sub> NI <sub>2</sub> .	Found.
N	3.60	3.56



of the above 2,5-diiod-6-nitrotoluene were reduced by warming for 18 hours at 60°–100° with a mixture of 84 grams of ferrous sulphate, 200 cc. of water, 200 cc. of concentrated ammonia, and a little alcohol. The solution was then filtered and the residue extracted with alcohol. On concentrating, the pure diiodtoluidine separated. The yield was 67 per cent. of the calculated. When crystallized from alcohol it formed colorless needles which melted sharply to an oil at 86°.

	Calculated for C <sub>7</sub> H <sub>7</sub> NI <sub>2</sub> .	Found.
N	3.90	3.87

When this material was diazotized, in the manner described above, and treated with potassium iodide a 90 per cent. yield of triiodtoluene was obtained. This triiodtoluene melted at  $80^{\circ}.5$ , crystallized from alcohol in lustrous needles and proved to be identical with the 2,3,6-triiodtoluene described above. When mixed with this material the melting point was not altered. This proves that 2-iod-*m*-acettoluide iodates in the 6 position and that iodine substitutes in the 3 or 5 position in 6-nitro-*o*-toluidine. The halogens usually take the para position to the amino group. That substitution takes place in the 5 position in this case was shown on removing the amino group from the iod-6-nitro-*o*-toluidine. The base was diazotized in dilute sulphuric acid and the solution was poured into hot alcohol. The mixture was warmed, made alkaline with sodium hydroxide and distilled with steam. A light yellow oil came over which, on cooling, solidified. This was not identical with 3-iod-6-nitrotoluene described by Artmann.<sup>1</sup> It must therefore be 5-iod-6-nitrotoluene, or, in other words, 2-nitro-3-iodtoluene. It formed, from petroleum ether, transparent, colorless, prismatic plates, which melted at  $65^{\circ}$ .

By SAMUEL R. SCHOLES.

4-Iod-*m*-toluidine,  $C_6H_3 \begin{matrix} \nearrow CH_3 \text{ (1)} \\ \searrow NH_2 \text{ (3)} \\ \quad \quad I \text{ (4)} \end{matrix}$ .—*p*-Acettoluide was the

starting point for the preparation of this and the following compounds. This was nitrated by the method of Cosack.<sup>2</sup> A cooling mixture is necessary to keep the temperature during the nitration at  $20^{\circ}$ – $30^{\circ}$ . The yield of material melting at  $93^{\circ}$  (3-nitro-*p*-acettoluide) was 85 per cent. of the calculated. The 3-nitro-*p*-toluidine was prepared from this material by warming with concentrated hydrochloric acid, 3 cc. of acid being used for each gram of acetyl compound. The base then separates on pouring into water, more completely on adding ammonia. It melted at  $115^{\circ}$ – $116^{\circ}$ . This base was diazotized and the solution treated with potassium iodide as described in previous cases. The yield of 4-iod-3-nitro-

<sup>1</sup> Monats. Chem., **26**, 1096.

<sup>2</sup> Ber. d. chem. Ges., **13**, 1088 (1880).

toluene, melting at  $55^{\circ}$ , was 84 per cent. of the calculated. This was reduced with ferrous sulphate and ammonia as follows: The iodinitrotoluene was treated with 10 times its weight (6.5 molecules) of ferrous sulphate, 20 times its weight of water, and an equal volume of concentrated ammonia. This mixture was allowed to stand at  $60^{\circ}$  for 12 hours and was then filtered. The residue was extracted with hot alcohol, and on evaporating the alcohol a green oil with a vile odor was obtained. This was distilled with steam and a pale brown oil came over. On cooling a portion below  $0^{\circ}$  the oil solidified; the remainder could then be induced to solidify at ordinary temperature by adding some of the solid. When this was crystallized from dilute alcohol, long, colorless needles, which melted constantly at  $38^{\circ}$ – $38^{\circ}.5$ , were obtained. The pure base has a disagreeable odor suggesting  $\alpha$ -naphthylamine. On standing several weeks it changed to a dark oil with a still more noticeable odor.

	Calculated for $C_7H_8NI$ .	Found.
N	6.01	5.95
I	54.80	54.56

In Beilstein's *Handbuch*<sup>1</sup> a substance is given, subject to interrogation, as 4-iod-3-toluidine, which melts at  $188^{\circ}$ – $189^{\circ}$ . This was obtained by Glassner.<sup>2</sup> We have prepared all of the four monoiod derivatives of *m*-toluidine and find that this substance does not agree with any of these compounds. When the work on this base was finished we discovered that Willgerodt and Simonis<sup>3</sup> had also prepared the compound by reducing 4-iod-3-nitrotoluene with ferrous sulphate. They give its melting point as  $48^{\circ}$ .

The *hydrochloride*,  $C_7H_8NI.HCl$ , is difficultly soluble in dilute hydrochloric acid, easily in hot alcohol, and undergoes hydrolysis in water. It decomposes on heating at  $155^{\circ}$  (Willgerodt and Simonis,  $90^{\circ}$ – $150^{\circ}$ ).

	Calculated for $C_7H_8NI.HCl$ .	Found.
N	5.19	5.12

<sup>1</sup> [3] 2, 475.

<sup>2</sup> Ber. d. chem. Ges., 8, 561.

<sup>3</sup> *Ibid.*, 39, 273 (1906).

The *thiourea derivative*,  $\text{C}_6\text{H}_5\cdot\text{I}\cdot\text{CH}_3\text{NHCSNHC}_6\text{H}_5$ , was formed on warming molecular quantities of the base and phenyl mustard oil on the steam bath in alcoholic solution. After three crystallizations from alcohol, in which it is difficultly soluble, it melted each time at  $162^\circ$ – $163^\circ$ .

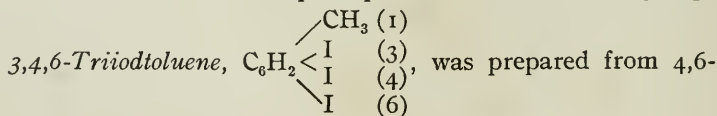
	Calculated for $\text{C}_{14}\text{H}_{13}\text{N}_2\text{IS}$ .	Found.
N	7.61	7.52

*4-Iod-m-acettoluide*, from the base and acetic anhydride, crystallized from alcohol in small, colorless, square-ended prisms melting at  $151^\circ$  ( $145^\circ$ – $146^\circ$ , Willgerodt and Simonis). It is only slightly soluble in water.

	Calculated for $\text{C}_9\text{H}_{10}\text{ONI}$ .	Found.
N	5.09	4.93

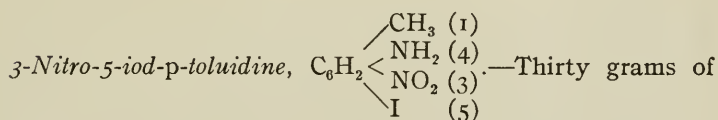
*Action of Iodine Monochloride*.—This acetyl derivative was mixed with the calculated quantity of iodine monochloride in glacial acetic acid and the solution warmed for a few minutes. The crystals which separated on cooling were recrystallized from alcohol. The material then melted at  $213^\circ$  and proved to be identical with the diiodacettoluide above, prepared by Hoffman. This shows that the compound is 4,6-diiod-*m*-acettoluide.

*Action of Iodine on 4-Iod-m-toluidine*.—Seven and seven-tenths grams of 4-iod-*m*-toluidine, 8.4 grams of iodine, 4 grams of calcium carbonate, 20 cc. ether and 10 cc. of water were mixed and warmed until the iodine disappeared. The product was then distilled in steam, whereupon 7.5 grams, or 63 per cent. of the calculated, of diiodtoluidine was obtained. On crystallizing from alcohol it melted at  $73^\circ$ – $74^\circ$  and when mixed with Hoffman's diiodtoluidine the melting point was not altered. From these experiments it is evident that in both 4-iod-*m*-acettoluide and the free base the iodine is substituted in the 6 or para position to the amino group.



diiod-*m*-toluidine by diazotizing and treating with potassium iodide as described in previous cases. It was difficult to diazotize the material by this method, owing to the insolubility of the sulphate. Ten grams of the base (not completely diazotized) gave 7 grams of triiodtoluene, or 60 per cent. of the calculated. It formed, from alcohol, long, slender, sharp-pointed, brownish needles, which melted to an oil at 119°-120°. It is almost completely nonvolatile in steam.

	Calculated for $C_7H_5I_3$ .	Found.
I	81.06	80.80



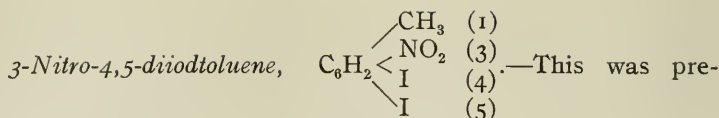
3-nitro-*p*-toluidine and 48 grams of iodine monochloride were mixed in 100 cc. of glacial acetic acid and warmed on the steam bath for 20-30 minutes. A better yield was obtained on warming than on standing. Water and bisulphite were added, whereupon a golden brown precipitate resulted. When this was crystallized from alcohol golden brown needles separated. They melted at 98°. The yield was 35 grams, or 68 per cent. of the calculated.

	Calculated for $C_7H_7O_2N_2I$ .	Found.
N	10.09	9.93

The position of the iodine in this compound was determined by acetylating the base. Acetic anhydride had no action, but when 1 gram of the base was treated with 2 cc. of acetyl chloride the mixture evolved heat and a white product was obtained, which, when crystallized from alcohol, gave colorless needles melting at 202°-203°. These proved to be identical with the iodnitro-*p*-acettoluide prepared by Wheeler and Liddle<sup>1</sup> by nitrating 3-iod-*p*-acettoluide. This settles the structure of this compound, which was left subject to interrogation in our previous paper.

<sup>1</sup> THIS JOURNAL, 42, 449 (1909).

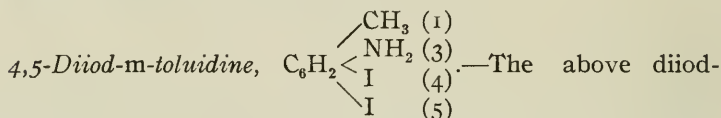




pared by diazotizing the above base and treating with potassium iodide in the usual manner. It crystallized from alcohol in orange, rectangular prisms, melting at  $84^\circ\text{--}85^\circ$ . The yield was 14 grams, or 64 per cent. of the calculated.

	Calculated for $\text{C}_7\text{H}_5\text{O}_2\text{NI}_2$ .	Found.
N	3.59	3.39
I	65.29	64.02

This compound is volatile with steam.



nitrotoluene (15 grams) was reduced with the calculated quantity of ferrous sulphate and an excess of ammonia by five hours' treatment at  $60^\circ$ . The black residue was then extracted with alcohol and an attempt was made to distil the extract in steam, but the base was not sufficiently volatile. The whole was gathered together in ether, dried over potassium hydroxide and the base was precipitated by passing dry hydrogen chloride into the solution. The gray-white precipitate (4.1 grams), after washing with ether, dissolved with difficulty in 95 per cent. alcohol and crystallized slowly in bunches of needles. The addition of a few drops of concentrated hydrochloric acid to the solution produced a more complete separation. On treating this hydrochloride with dilute ammonia the base was obtained as an oil which soon solidified. It was separated from traces of tar by repeated crystallization from dilute alcohol. It formed an extremely bulky mass of colorless, cottonlike needles, which finally melted to an amber-colored oil at  $66^\circ\text{--}67^\circ$ .

	Calculated for $\text{C}_7\text{H}_7\text{NI}_2$ .	Found.
N	3.90	3.67

This base was converted by the action of iodine into an amorphous brown-black substance, which had no definite melting point. The product was neither a tri- nor tetraiod-toluidine.

*4,5-Diiod-m-acettoluide*,  $C_6H_2CH_3I_2NHCOCCH_3$ , from the base and acetyl chloride, is very difficultly soluble in water and readily in alcohol. It formed short, colorless needles, melting at  $183^{\circ}$ – $184^{\circ}$ , when repeatedly crystallized from alcohol (analysis I).

	Calculated for $C_6H_5ONI_2$ .	I.	Found. II.
N	3.50	3.22	3.84

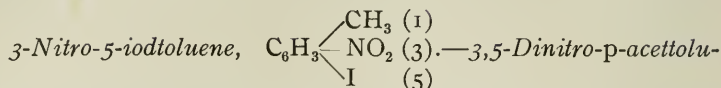
When this acetyl derivative was treated with the calculated quantity of iodine monochloride in glacial acetic acid and allowed to stand overnight, unaltered material separated. It formed needles as before and melted at  $183^{\circ}$ – $184^{\circ}$  after crystallizing from alcohol.

When warmed (2.2 grams) in glacial acetic acid with an excess of iodine monochloride ( $5ICl$ ), the material obtained had a different appearance. On crystallizing from alcohol it then separated in small diamond-shaped blocks which melted at  $200^{\circ}$ – $201^{\circ}$ . Two more recrystallizations failed to change the melting point. A nitrogen determination (analysis II by Brautlecht) indicated that it was a diiodacettoluide, or unaltered material.

We have prepared all of the six theoretically possible diiod-*m*-acettoluides, with the exception of 2,4-diiod-*m*-acettoluide. 2,6-Diiod-*m*-acettoluide melts at  $171^{\circ}$ ; 2,5-diiod-*m*-acettoluide at  $198^{\circ}$ ; <sup>1</sup> 4,6-diiod-*m*-acettoluide at  $213^{\circ}$ , and 5,6-diiod-*m*-acettoluide at  $208^{\circ}$ .<sup>1</sup> When the last three isomers were mixed with the above material, melting at  $200^{\circ}$ , the mixture in each case melted below  $175^{\circ}$ . This shows that the substance did not undergo a rearrangement into any of these isomers. Whether or not the lower melting point ( $183^{\circ}$ – $184^{\circ}$ ) was caused by some impurity which tenaciously adhered to the material will have to be decided later. The amount of substance melting at  $200^{\circ}$  was too small for saponi-

<sup>1</sup> To be described in a following paper.

fication and subsequent purification and identification of the base.

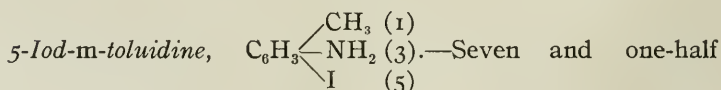


ide was prepared by the method of Jackson and Ittner<sup>1</sup> and saponified by boiling with 50 per cent. sulphuric acid.

We found that the most convenient method for the removal of the amino group was as follows: Twenty grams of the base were suspended in a mixture of 20 cc. of concentrated sulphuric acid and 150 cc. of absolute alcohol. The mixture was heated on the steam bath and 16 grams of powdered sodium nitrite were slowly added. After heating 30 minutes no red particles of the base were visible. On pouring into water a yellow precipitate separated, which, when crystallized from alcohol, melted at  $88^\circ\text{--}91^\circ$ . The yield was 12 grams, or 70 per cent. of the calculated.

The 3,5-dinitrotoluene thus obtained was reduced to 5-nitro-m-toluidine by means of ammonium sulphide.<sup>2</sup> When this base (9 grams) was diazotized and treated with potassium iodide in the manner described above in other cases, the reaction proceeded smoothly, and, after crystallizing the product from alcohol, 7.5 grams of yellow, rectangular prisms melting at  $77^\circ$  were obtained.

	Calculated for $\text{C}_7\text{H}_6\text{O}_2\text{NI}$ .	Found.
N	5.34	5.00



grams of the above nitroiodtoluene, 50 grams of crystallized ferrous sulphate, 200 cc. of water and 200 cc. of concentrated ammonia were mixed and warmed for 24 hours. The mixture was then distilled in steam; an oil came over which readily solidified and dissolved completely in dilute hydrochloric acid. On crystallizing from petroleum ether, long, colorless,

<sup>1</sup> THIS JOURNAL, **19**, 5 (1897).

<sup>2</sup> Neville and Winther: Ber. d. chem. Ges., **15**, 2985.

asbestoslike needles, which melted at  $78^{\circ}$ – $78^{\circ}.5$ , were obtained. The yield was about 3 grams.

	Calculated for $C_7H_9NI$ .	Found.
N	6.02	5.89

This iod-*m*-toluidine has a very faint odor, suggesting that of  $\alpha$ -naphthylamine, and can be kept for months without change. The acetyl derivative forms mica-like plates from alcohol which melt at  $183^{\circ}$ .

NEW HAVEN, CONN.,  
April, 1910.

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## A STUDY OF THE SURFACE TENSIONS OF SOME UNSATURATED ORGANIC COMPOUNDS.

BY FREDERICK H. GETMAN.

In recent years the attention of workers in this laboratory has been largely directed to the investigation of the chemical behavior of unsaturated organic compounds. As a result of this continued and systematic research many new substances have been prepared and important generalizations have been pointed out.

Notwithstanding the large accumulation of chemical data concerning unsaturated organic compounds, however, very little has been done in the way of determining their physical constants.

The value of the systematic determination of physical constants of organic compounds has already become recognized and we believe that the careful measurement of a number of physical constants of the typical unsaturated compounds which have been studied in this and other laboratories will prove valuable aids to the future study of these interesting substances.

In Stewart's "Recent Advances in Physical and Inorganic Chemistry,"<sup>1</sup> we find the following significant passage at the conclusion of the chapter on Absorption Spectra:<sup>2</sup> "There are two classes of workers whose researches are tending to bring spectroscopy into touch with chemical problems. The

<sup>1</sup> Published by Longmans, Green & Co.

<sup>2</sup> p. 156.

first of these concern themselves with the relation between spectroscopic measurements and other physical properties of organic substances, such as refractive index, optical rotatory power, magnetic rotation, and so forth.

"The second class of investigators endeavor to link their spectroscopic results with their chemical reactions in order to find out whether there be any connection traceable between the two phenomena.

"In either of these directions there appears to be a fruitful field awaiting research."

It is our opinion that what has been said of spectroscopy and its relation to chemical problems is equally applicable to any other line of physical measurement. Before any trustworthy relations can be established a large amount of physical data must be collected and any attempts at generalization must be made with caution.

Through the work of Ramsay and Shields,<sup>1</sup> Ramsay and Aston,<sup>2</sup> Renard and Guye,<sup>3</sup> and others, the importance of surface tension measurements as a criterion of molecular complexity has been emphasized.

It has seemed advisable therefore to undertake a systematic investigation of the surface tensions of a series of closely related unsaturated organic compounds.

The substances which have been studied are mesityl oxide,  $\beta$ -dimethylacrylic acid, benzalacetone, benzalmethylethyl ketone, and benzalpinacolin.

#### *Method and Apparatus.*

(a) *Surface Tension.*—The surface tension of a liquid, expressed in dynes per centimeter, may be obtained by means of the familiar formula

$$\gamma = 1/2hrg(d-\sigma) \quad (1),$$

where  $h$  = capillary elevation in centimeters,

$r$  = radius of capillary in centimeters,

$d$  = density of liquid,

$\sigma$  = density of vapor of liquid,

$g$  = acceleration due to gravity.

<sup>1</sup> Z. physik. Chem., **12**, 433 (1893).

<sup>2</sup> *Ibid.*, **15**, 89 (1894).

<sup>3</sup> J. chim. phys., **5**, 81 (1907).



Except for measurements of extreme precision the density of the vapor of the liquid may be omitted and the formula may be written thus:

$$\gamma = 1/2hrdg \quad (2).$$

The capillary method for the determination of surface tension has been used with success by numerous investigators, among whom may be mentioned Ramsay and Shields, Renard and Guye, and Przyluska.<sup>1</sup>

The apparatus which I have employed in this investigation is a modified form of that used by Mlle. Przyluska. The assembled apparatus is shown in Fig. I. The capillary tube *C*, having been carefully selected so as to insure as uniform bore as possible, was supported by means of a piece of glass rod, *D*, bent as shown in the illustration. The rod was sealed to the side of *C*, thus preventing drops of condensed liquid from closing the upper end of the capillary. The rod *D* passed tightly through a hole in the stopper closing the test tube *B*. Through this same stopper passed a thermometer, *F*, and a tube, *E*, bent at right angles. By blowing gently through *E* the liquid in *B* could be forced up into the capillary, thus insuring thorough wetting of the walls before reading the elevation. The tube *B* was placed inside the vapor jacket *A*, in which various liquids were boiled, thus maintaining *B* and its contents at a definite temperature. The side tube *G* served to connect the vapor jacket with a condenser.

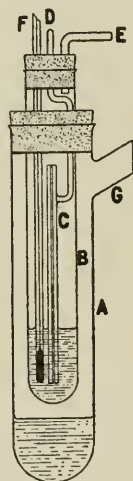


Fig. I.

The capillary elevation of the liquid was measured by means of a cathetometer. By means of a plummet the capillary tube was rendered as nearly vertical as possible.

The following liquids were used in the vapor jacket:

	Boiling point.		Boiling point.
Acetone	55°	Xylene (commercial)	135°
Methyl alcohol	66°	Brombenzene	155°
Benzene	80°	Aniline	182°
Toluene	109°	Methyl benzoate	199°
Amyl formate	116°	Acetophenone	202°

<sup>1</sup> Przyluska: J. chim. phys., 7, 511 (1909).

The calibration of the capillary was effected with pure benzene, obtained from Kahlbaum, warranted to be free from thiophene. The capillary was first washed with concentrated nitric acid and then with potassium hydroxide, after which it was washed with chromic acid and then with conductivity water. The tube was dried by means of a slow current of air bubbled through concentrated sulphuric acid.

About 10 cc. of benzene were introduced into the tube *B* and after the apparatus had acquired room temperature, readings of the temperature and capillary elevation were taken at frequent intervals during half an hour.

The capillary elevation was then determined in the vapors of boiling acetone and of boiling methyl alcohol, the readings being repeated over a period of several hours. The surface tension and the density of benzene at several temperatures was obtained from the tables of Landolt and Börnstein and the measurements of Ramsay and Shields, Ramsay and Aston, Renard and Guye, and Morgan and Stevenson.<sup>1</sup> Taking the value of *g*, the acceleration due to gravity, to be 980.2, the value of *r* was calculated by means of the formula

$$r = \frac{2\gamma}{hdg} \quad (3).$$

The results of the calibration are given in Table I, each value of *h* being the mean of several determinations. The mean value of the radius of the tube, 0.02241 cm., was checked by the well-known method of weighing out with mercury, and the agreement was satisfactory:

Table I.

Temp.	<i>h</i> .	<i>d</i> .	<i>r</i> .	<i>r</i> .
22°.0	2.91	0.8755	27.83	0.02229
57°.0	2.53	0.8376	23.37	0.02251
64°.5	2.46	0.8295	22.42	0.02242

Mean, 0.02241

(*b*) *Density*.—The densities have been determined by means of a weight dilatometer shown in Fig. II. The dilatom-

<sup>1</sup> Z. physik. Chem., **63**, 151 (1908).

eter, nearly filled with mercury, was placed in the vapor jacket shown in Fig. I. When the mercury and dilatometer had acquired the temperature of the surrounding vapor, more mercury was added until the level of the mercury column remained coincident with the mark *M* on the stem of the dilatometer.

At least half an hour was allowed for the establishment of thermal equilibrium. The dilatometer was then removed from the vapor jacket and allowed to cool to the temperature of the room. It was then placed in a tared beaker on the pan of the balance and, after acquiring the temperature of the balance case, was weighed.

The density of mercury at the temperature of the vapor jacket was obtained from the tables of Landolt and Börnstein. Having the mass of the mercury in the dilatometer and knowing its density, the volume of the dilatometer at the temperature of the vapor jacket was calculated. Similarly for a series of temperatures the corresponding volumes of the dilatometer were determined. The results of this calibration are given in Table II, in which *m* denotes the mass of mercury in the dilatometer, *d* the density of the mercury, and *v* the volume corresponding to the temperature given in the first column:



Fig. II.

Table II.

Temp.	<i>m.</i>	<i>d.</i>	<i>v = m/d.</i>
18°.0	39.3215	13.5511	2.9017
111°.0	38.7490	13.3259	2.9078
122°.5	38.6765	13.2984	2.9085
155°.0	38.4837	13.2212	2.9111
197°.0	38.2415	13.1219	2.9143

In the determination of densities with the weight dilatometer the process was identical with<sup>sc</sup> that used in the calibration.

The substance was placed in the dilatometer and brought to the mark at the different temperatures, the dilatometer being weighed after adjustment for each temperature. From the calibration curve the volume corresponding to each temperature could be read off and the density thus calculated.

In the case of mesityl<sup>al</sup>oxide, which is a liquid at ordinary

temperatures, the Sprengel-Ostwald pycnometer was used for density determinations. The densities were calculated by means of the formula

$$d_{4^{\circ}}^{t^{\circ}} = \frac{w_1}{w_2} (Q - 0.0012) + 0.0012 \quad (4),$$

where  $d_{4^{\circ}}^{t^{\circ}}$  = density of liquid at  $t^{\circ}$  referred to water at  $4^{\circ}$ ,

$w_1$  = weight of liquid,

$w_2$  = weight of equal volume of water,

$Q$  = density of water at  $t^{\circ}$ ,

0.0012 = density of air.

(c) *Temperature*.—All of the thermometers used in this investigation were carefully compared with Reichsanstalt standard No. 5771 and proper corrections were introduced where necessary.

*Calculation of Association*.—It has been shown by Ramsay and Shields<sup>1</sup> that the molecular surface tension of a liquid is given by the formula

$$\gamma(Mv)^{\frac{2}{3}} = k(t_c - t - \delta) \quad (5),$$

where  $M$  denotes the molecular weight,  $v$  the volume of a gram of the liquid at the temperature of the experiment,  $t_c$  the critical temperature,  $t$  the temperature of the experiment, and  $k$  the coefficient of variation of molecular surface tension, which has been shown to be about 2.12 for normal or non-associated liquids. The coefficient  $k$  may be calculated from the surface tension data at two different temperatures, thus:

$$k = \frac{\gamma_1(Mv_1)^{\frac{2}{3}} - \gamma_2(Mv_2)^{\frac{2}{3}}}{t_2 - t_1} \quad (6);$$

or substituting  $1/d$  for  $v$ , where  $d$  is the corresponding density, we have

$$k = \frac{\gamma_1\left(\frac{M}{d_1}\right)^{\frac{2}{3}} - \gamma_2\left(\frac{M}{d_2}\right)^{\frac{2}{3}}}{t_2 - t_1} \quad (7).$$

Should the value of  $k$  be less than 2.12 it is an indication of

<sup>1</sup> *Loc. cit.*

molecular association. The degree of association,  $x$ , may be calculated by means of the formula

$$x = \left( \frac{2.12}{k} \right)^{3/2} \quad (8).$$

*Materials.*—The substances used in this investigation have already been mentioned. They were mesityl oxide,  $\beta$ -dimethylacrylic acid, benzalacetone, benzalmethylethyl ketone and benzalpinacolin. With the exception of mesityl oxide all of these substances are solids at ordinary temperatures. The mesityl oxide was purified by vacuum distillation until no residue remained in the distilling flask. The other substances were purified by careful vacuum distillation and subsequent recrystallization. The recrystallization was repeated until hardly a trace of yellow color remained. It gives me pleasure to acknowledge my indebtedness to Professor E. P. Kohler for the preparation and purification of these substances. After the four solid substances had been purified their melting points were very carefully determined. In each case enough material was taken to give about 10 cc. of liquid when melted. The substance was placed in a test tube fitted with a ring stirrer and a thermometer, and the whole placed in a large beaker of water, also furnished with a stirrer and thermometer. The water was warmed by means of a Bunsen burner until the substance in the test tube had fused, when the source of heat was removed and the system was allowed to cool, both stirrers being agitated simultaneously. The thermometer was read at frequent intervals until the mass solidified and a constant temperature was attained. In all cases there was overcooling to the extent of about  $1^\circ$ . The following melting points were obtained:

	Melting point.
$\beta$ -Dimethylacrylic acid	$69^\circ.2$
Benzalacetone	$40^\circ.2$
Benzalmethylethyl ketone	$37^\circ.5$
Benzalpinacolin	$39^\circ.5$

*Tabulation of Results.*—The results obtained are recorded in the following tables. Tables III–VII, inclusive, give the den-



sities of the five substances investigated. In Tables III and IV the densities actually determined are recorded, while Tables V, VI and VII are compiled from the smoothed curve plotted (Fig. III) from the experimental data. Tables VIII-XVII contain the surface tension data. In

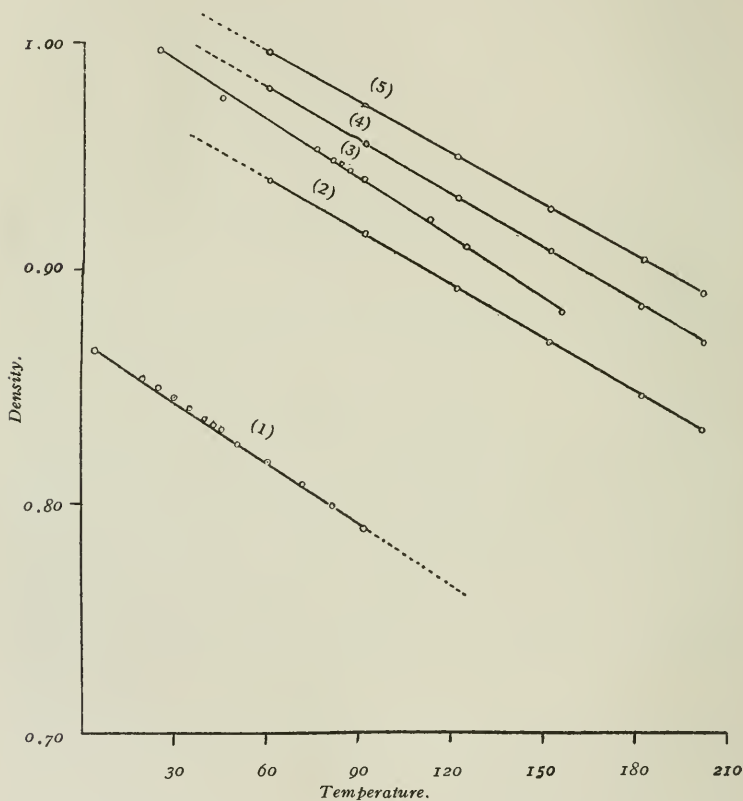


Fig. III.

- (1) Mesityl oxide. (2) Benzalpinacolin. (3)  $\beta$ -Dimethylacrylic acid. (4) Benzal-methylethyl ketone. (5) Benzalacetone.

these tables  $h$  denotes the observed capillary elevation in centimeters,  $d$  the density,  $\gamma$  the surface tension in dynes per centimeter, and  $k_1$  and  $k_2$  the coefficient of variation of molecular surface tension calculated by means of

equation (7). In the calculation of these coefficients two methods have been followed. In the first method, the coeffi-

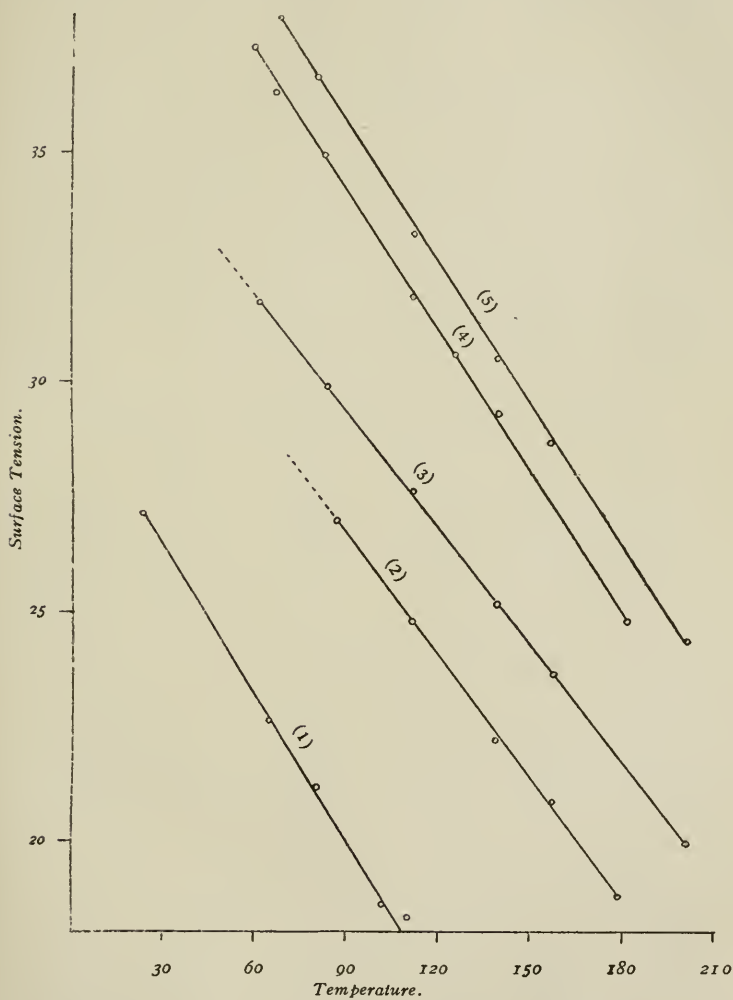


Fig. IV.

- (1) Mesityl oxide. (2)  $\beta$ -Dimethylacrylic acid. (3) Benzalpinacolin. (4) Benzal-methylethyl ketone. (5) Benzalacetone.

cient  $k_1$  was obtained by taking the difference between consecutive molecular surface tensions and dividing by the tem-

perature interval between which the capillary elevations were measured: in the second method the coefficient  $k_2$  was obtained by taking the difference between each molecular surface tension and the first molecular surface tension in the table and dividing by the corresponding temperature interval. It will be observed that the value of the coefficient obtained by the second method is more nearly constant than that obtained by the first method. This same observation was made by Mlle. Przyluska<sup>1</sup> in her investigation of the molecular complexity of diphenylamine and triphenylmethane. In Table XI, where  $k_1$  and  $k_2$  are considerably smaller than 2.12, the molecules are associated. The extent of this association  $x$  is calculated by means of equation (8).

The surface tensions are plotted in Fig. IV.

Table III.—*Mesityl Oxide*,  $(\text{CH}_3)_2\text{C} : \text{CHCOCH}_3$ .

Temp.	<i>d.</i>	Temp.	<i>d.</i>	Temp.	<i>d.</i>
5°.0	0.8662	35°.0	0.8422	50°.0	0.8267
20°.2	0.8545	40°.0	0.8385	60°.0	0.8189
25°.0	0.8510	42°.5	0.8357	70°.0	0.8091
30°.0	0.8462	45°.0	0.8332	80°.0	0.7998
				90°.0	0.7898

Table IV.—*β-Dimethylacrylic Acid*,  $(\text{CH}_3)_2\text{C} : \text{CH}.\text{CO}_2\text{H}$ .

Temp.	<i>d.</i>	Temp.	<i>d.</i>	Temp.	<i>d.</i>
24°.4	1.0062	80°.0	0.9481	95°.0	0.9360
25°.0	0.9959	82°.0	0.9474	111°.0	0.9225
45°.0	0.9750	85°.0	0.9438	122°.5	0.9115
75°.0	0.9538	90°.0	0.9409	154°.0	0.8825

Table V.—*Benzalacetone*,  $\text{C}_6\text{H}_5.\text{CH} : \text{CH}.\text{CO}.\text{CH}_3$ .

Temp.	<i>d.</i>	Temp.	<i>d.</i>	Temp.	<i>d.</i>
60°	0.9947	110°	0.9573	160°	0.9202
70°	0.9871	120°	0.9500	170°	0.9129
80°	0.9796	130°	0.9424	180°	0.9054
90°	0.9721	140°	0.9352	190°	0.8981
100°	0.9648	150°	0.9278	200°	0.8908

<sup>1</sup> *Loc. cit.*

Table VI.—Benzalmethylethyl Ketone,  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{C}_2\text{H}_5$ .

Temp.	d.	Temp.	d.	Temp.	d.
50°	0.9867	100°	0.9478	150°	0.9087
60°	0.9789	110°	0.9399	160°	0.9010
70°	0.9710	120°	0.9321	170°	0.8932
80°	0.9630	130°	0.9243	180°	0.8856
90°	0.9553	140°	0.9165	190°	0.8775
				200°	0.8697

Table VII.—Benzalpinacolin,  $\text{C}_6\text{H}_5 \cdot \text{CH} : \text{CH} \cdot \text{CO} \cdot \text{C}(\text{CH}_3)_3$ .

Temp.	d.	Temp.	d.	Temp.	d.
60°	0.9394	110°	0.9009	160°	0.8623
70°	0.9318	120°	0.8932	170°	0.8547
80°	0.9240	130°	0.8855	180°	0.8470
90°	0.9162	140°	0.8779	190°	0.8392
100°	0.9087	150°	0.8701	200°	0.8341

Table VIII.—Mesityl Oxide,  $(\text{CH}_3)_2\text{C} : \text{CHCOCH}_3$ .

Temp.	h.	d.	r.
24°.0	2.90	0.8515	27.12
64°.5	2.53	0.8145	22.63
79°.0	2.41	0.8005	21.17
100°.0	2.19	0.7800	18.56
108°.5	2.16	0.7712	18.29
122°.0	1.92	0.7590	16.01

Table IX.

Temp.	r (corrected).	k <sub>1</sub> .	k <sub>2</sub> .
20°	27.55	...	...
40°	25.35	2.23	2.23
60°	23.15	2.18	2.20
80°	20.95	2.27	2.22
100°	18.76	2.30	2.24
120°	16.55	2.42	2.28
Mean,		2.28	2.22

Table X.—β-Dimethylacrylic Acid,  $(\text{CH}_3)_2\text{C} : \text{CH} \cdot \text{CO}_2\text{H}$ .

Temp.	h.	d.	r.
85°	2.60	0.9450	26.98
110°	2.45	0.9220	24.80
137°	2.25	0.8980	22.19
155°	2.15	0.8820	20.83
177°	1.98	0.8620	18.74

Table XI.

Temp.	$\gamma$ (corrected).	$k_1$ .	$k_2$ .	$x$ .
85°	26.98	....	....	....
110°	24.75	1.61	1.52	1.52
137°	22.33	1.71	1.38	1.38
155°	20.70	1.77	1.31	1.31
137°	18.74	1.78	1.29	1.29

Table XII.—Benzalacetone,  $C_6H_5CH : CH.CO.CH_3$ 

Temp.	$h$ .	$d$ .	$\gamma$ .
60°.0	3.53	0.9947	38.53
67°.8	3.49	0.9889	37.89
80°.0	3.40	0.9796	36.58
110°.5	3.15	0.9570	33.11
137°.5	2.96	0.9370	30.46
155°.0	2.82	0.9240	28.62
199°.0	2.49	0.8914	24.37

Table XIII.

Temp.	$\gamma$ (corrected).	$k_1$ .	$k_2$ .
60°	38.53	....	....
80°	36.50	2.25	2.25
100°	34.47	2.39	2.34
120°	32.42	2.44	2.39
140°	30.39	2.45	2.39
160°	28.35	2.40	2.42
180°	26.30	2.70	2.44
200°	24.25	2.64	2.47
Mean,		2.47	2.40

Table XIV.—Benzalmethylethyl Ketone,  $C_6H_5.CH : CH.CO.C_2H_5$ 

Temp.	$h$ .	$d$ .	$\gamma$ .
59°.5	3.46	0.9795	37.21
67°.0	3.39	0.9735	36.24
82°.0	3.30	0.9615	34.84
110°.5	3.08	0.9395	31.78
124°.0	2.99	0.9290	30.51
138°.0	2.90	0.9182	29.24
180°.0	2.55	0.8856	24.79



Table XV.

Temp.	$r$ (corrected).	$k_1$ .	$k_2$ .
50°	38.05	....	....
80°	35.00	2.46	2.46
100°	32.97	2.55	2.50
120°	30.94	2.55	2.52
140°	28.93	2.60	2.54
160°	26.87	2.73	2.57
180°	24.79	2.82	2.61
Mean,		2.62	2.53

Table XVI.—Benzalpinacolin,  $C_6H_5 \cdot CH : CH \cdot CO \cdot C(CH_3)_3$ .

Temp.	$h$ .	$d$ .	$r$ .
62°.0	3.08	0.9380	31.70
83°.0	2.95	0.9216	29.86
110°.3	2.79	0.9006	27.59
137°.1	2.60	0.8800	25.13
156°.0	2.49	0.8654	23.66
199°.0	2.18	0.8320	19.92

Table XVII.

Temp.	$r$ (corrected).	$k_1$ .	$k_2$ .
60°	31.85	....	....
80°	30.10	2.40	2.40
100°	28.40	2.41	2.41
120°	26.70	2.44	2.42
140°	24.98	2.68	2.48
160°	23.26	2.44	2.48
180°	21.52	2.65	2.50
200°	19.80	2.73	2.53
Mean,		2.53	2.46

## DISCUSSION OF RESULTS.

An inspection of the foregoing tables shows that, with the exception of  $\beta$ -dimethylacrylic acid, all of the substances studied are nonassociated. This conclusion receives confirmation through an application of the empirical formula proposed by Longinescu<sup>1</sup> as a test for molecular association.

If we denote the absolute melting point of a compound by

<sup>1</sup> Ann. Sci Univ. Jassy, 1, 359. J. chim. phys., 1, 289, 296 (1903).

$T$  and its density in the solid state by  $d$ , the number  $n$  of atoms in the molecule may be computed by means of the formula

$$n = \left( \frac{T}{70d} \right)^2.$$

In like manner  $n$  may be calculated by means of the formula

$$n = \left( \frac{T'}{100d'} \right)^2,$$

where  $T'$  denotes the absolute boiling point and  $d'$  the density at  $0^\circ$ .

The subjoined table gives the value of  $n$  calculated by means of Longinescu's formulas and also the value obtained by counting the number of atoms in the chemical formula for a single molecule:

Substance.	Density.	Abs. m. p.	$n$ .	$n$ (calc.).
$(\text{CH}_3)_2\text{C} : \text{CH}.\text{CO}.\text{CH}_3$	0.8700	403.0 (b. p.)	17	21
$(\text{CH}_3)_2\text{C} : \text{CH}.\text{CO}_2\text{H}$	0.9590	342.2	15	25
$\text{C}_6\text{H}_5\text{CH} : \text{CH}.\text{CO}.\text{CH}_3$	1.0095	313.2	21	20
$\text{C}_6\text{H}_5\text{CH} : \text{CH}.\text{CO}.\text{C}_2\text{H}_5$	0.9965	310.5	24	20
$\text{C}_6\text{H}_5\text{CH} : \text{CH}.\text{CO}.\text{C}(\text{CH}_3)_3$	0.9550	312.5	30	22

It will be seen that these results are in complete agreement with those obtained from the surface tension data.

The value of  $k$  for the nonassociated compounds is in all cases greater than 2.12, the mean value assigned by Ramsay and Shields.

The average values of  $k$  for the four nonassociated substances studied are 2.22, 2.40, 2.53, and 2.46, respectively.

It will also be noticed that the association of  $\beta$ -dimethylacrylic acid slowly decreases with increase in temperature.

Much more data must be collected before it will be possible to establish any connection between the chemical and physical properties of this class of compounds. It is our intention to continue this line of investigation in the near future.

BRYN MAWR COLLEGE,  
BRYN MAWR, PA.,  
May, 1910.

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# THE CONDUCTIVITY AND DISSOCIATION OF ORGANIC ACIDS IN AQUEOUS SOLUTION AT DIFFERENT TEMPERATURES.

BY GEORGE F. WHITE AND HARRY C. JONES.

In our preliminary article<sup>1</sup> results were given for the conductivity of several organic acids at temperatures ranging from 0° to 35°. This work has been extended, and complete data are here presented for the conductivity and likewise the dissociation of all the acids worked with.

$\mu_{\infty}$  for *Sodium Chloride*.—In order to obtain  $\mu_{\infty}$  for the organic acids to calculate their dissociation, the method which involves the use of the sodium salts of these acids, based on Kohlrausch's law of the independent migration velocities of ions, was resorted to. Thus, to calculate  $\mu_{\infty}$  for acetic acid, for instance, the following equation suffices:

$$\mu_{\infty}(\text{HOOCCH}_3) = \mu_{\infty}(\text{HCl}) + \mu_{\infty}(\text{NaOOCCH}_3) - \mu_{\infty}(\text{NaCl}),$$

in which  $\mu_{\infty}$  is the limiting conductivity for each substance. The following table gives the conductivity of sodium chloride solutions between 0° and 35°:

<i>Sodium Chloride.</i>				
V.	$\mu_v$ 0°.	$\mu_v$ 12°.13.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	57.17	79.69	106.2	128.6
128	59.76	83.96	112.3	137.2
512	62.01	87.54	117.0	142.1
1024	62.80	88.58	118.4	143.7
2048	*63.04	88.98	*118.8	*144.0

The following equation was calculated by means of values marked with an asterisk in the table:

$$\mu_{\infty} = 63.04 + 2.04t - 0.00823t^2.$$

$\mu_{2048}$  at 12°.13 calculated from this equation gave 88.99, while the observed value was 88.98.

$\mu_{\infty}$  for *Hydrochloric Acid*.—Following is a table which served to give the limiting conductivities of hydrochloric acid.

<sup>1</sup> THIS JOURNAL, 42, 520 (1909).

*Hydrochloric Acid.*

V.	$\mu_v$ 0°.	$\mu_v$ 14°.82.	$\mu_v$ 25°.	$\mu_v$ 35°.
128	240.7	326.6	384.9	438.0
512	245.4	332.3	392.0	448.0
1024	343.0	331.0	387.1	444.7

The maximum conductivity was taken as  $\mu_{512}$ , and varies according to the following equation:

$$\mu_{\infty} = 245.4 + 6.06t - 0.00776t^2.$$

$\mu_{512}$  at 14°.82, calculated from the equation, gave 331.1, as against 331.0 observed.

$\mu_{\infty}$  for the Sodium Salts of the Organic Acids.—Ostwald<sup>1</sup> obtained  $\mu_{\infty}$  for the sodium salt of the organic acids by calculating the difference between the conductivity of sodium chloride at a certain dilution, *e. g.*,  $V = 32$ , and at infinite dilution. This difference he assumed to be constant for all sodium salts, and, therefore, by adding it to the conductivity of the sodium salt of any acid at the dilution  $V = 32$ ,  $\mu_{\infty}$  for that acid would be obtained. Instead of using this method in this investigation,  $\mu_{\infty}$  for the sodium salts was determined directly from conductivity measurements, which are given in the following tables:

*Sodium Acetate.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
1024	43.35	62.10	84.82	104.9
2048	44.56	63.83	87.69	107.9
4096	44.60	63.92	87.64	106.8

$$\mu_{\infty} = 44.56 + 1.520t + 0.00822t^2.$$

*Sodium Propionate.*

V.	$\mu_v$ 0°.	$\mu_v$ 13°.57.	$\mu_v$ 25°.	$\mu_v$ 35°.
1024	39.82	59.63	78.60	96.86
2048	40.57	60.99	81.00	100.6
4096	40.58	60.91	81.03	100.8

$$\mu_{\infty} = 40.57 + 1.378t + 0.00959t^2.$$

*Sodium Butyrate.*

V.	$\mu_v$ 0°.	$\mu_v$ 13°.07.	$\mu_v$ 25°.	$\mu_v$ 35°.
1024	39.33	58.11	77.69	96.39
2048	40.51	60.29	80.95	100.2
4096	40.54	60.20	80.86	100.1

$$\mu_{\infty} = 40.51 + 1.401t + 0.00868t^2.$$

<sup>1</sup> Z. physik. Chem., 2, 840 (1888).

*Sodium Hippurate.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
1024	35.65	51.30	70.77	86.74
2048	36.23	52.07	71.54	87.98
4096	36.31	52.00	71.60	88.20

$$\mu_{\infty} = 36.23 + 1.250t + 0.00651t^2.$$

*Sodium Salts of the Toluic Acids.*

V.	$\mu_v$ 0°.				$\mu_v$ 12°.			
	Ortho.	Meta.	Para.	$\alpha$ .	Ortho.	Meta.	Para.	$\alpha$ .
1024	37.82	38.02	38.02	37.89	54.45	54.49	54.41	54.42
2048	38.26	38.25	38.25	38.26	55.05	55.00	55.23	54.87
4096	38.18	38.28	38.28	38.27	54.99	55.09	55.43	54.80

V.	$\mu_v$ 25°.				$\mu_v$ 35°.			
	Ortho.	Meta.	Para.	$\alpha$ .	Ortho.	Meta.	Para.	$\alpha$ .
1024	74.04	74.33	74.90	73.90	91.87	92.16	91.93	91.98
2048	70.48	75.63	75.44	75.46	92.68	92.88	92.40	92.70
4096	74.92	75.59	75.28	75.11	92.58	92.79	92.29	92.29

$$\mu_{\infty} (\alpha \text{ acid}) = 38.26 + 1.320t + 0.00674t^2.$$

*Sodium Cinnamate.*

V.	$\mu_v$ 0°.	$\mu_v$ 13° .07.	$\mu$ 25°.	$\mu_v$ 35°.
1024	27.15	54.59	72.86	89.91
2048	37.69	55.60	74.49	92.06
4096	37.60	55.78	74.41	91.95

$$\mu_{\infty} = 37.69 + 1.271t + 0.00811t^2.$$

*Sodium Salicylate.*

V.	$\mu_v$ 0°.	$\mu_v$ 12° .32.	$\mu_v$ 25°.	$\mu_v$ 35°.
1024	40.02	57.77	78.09	96.21
2048	40.55	58.58	79.97	98.90
4096	40.56	58.57	80.00	98.90

$$\mu_{\infty} = 40.51 + 1.353t + 0.00902t^2.$$

*Sodium Sulphanilate.*

V.	$\mu_v$ 0°.	$\mu_v$ 11° .90.	$\mu_v$ 25°.	$\mu_v$ 35°.
1024	38.47	55.37	76.20	93.81
2048	39.52	56.28	77.69	96.05
4096	39.36	56.34	77.70	95.85

$$\mu_{\infty} = 39.52 + 1.307t + 0.00879t^2.$$

Since, as shown by these results, the above salts give maximum conductivities at  $V = 2048$ , the remaining salts were measured only at this dilution.



*Sodium Mandelate.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
2048	38.25	55.00	76.00	93.20
	$\mu_\infty = 38.25 + 1.296t + 0.00856t^2.$			

*Sodium Crotonate.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
2048	39.53	57.25	79.00	97.03
	$\mu_\infty = 39.53 + 1.416t + 0.00639t^2.$			

*Sodium Pyromucate.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
2048	40.89	59.30	81.84	100.5
	$\mu_\infty = 40.89 + 1.478t + 0.00639t^2.$			

*Sodium Benzoate (solution of dry salt).*

V.	$\mu_v$ 0°.	$\mu_v$ 14°.54.	$\mu_v$ 25°.	$\mu_v$ 35°.
2048	38.93	60.25	77.69	96.04
	$\mu_\infty = 38.93 + 1.348t + 0.00811t^2.$			

*Sodium Benzoate (by titration).*

V.	$\mu_v$ 0°.	$\mu_v$ 14°.54.	$\mu_v$ 25°.	$\mu_v$ 35°.
2048	38.91	60.33	77.73	96.25

*Sodium Gallate.*

V.	$\mu_v$ 0°.	$\mu$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
2048	37.91	54.50	74.38	91.80
	$\mu_\infty = 37.91 + 1.259t + 0.00799t^2.$			

*Sodium o-Aminobenzoate.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
2048	38.20	54.81	75.26	92.51
	$\mu_\infty = 38.20 + 1.308t + 0.00696t^2.$			

Solutions of those sodium salts obtainable from Kahlbaum were made up by weighing out the dry, *purified salt*, while the remainder were prepared by titrating a solution of the free organic acid with a solution of caustic soda. That this alkali contained no appreciable amount of carbonate was proved by comparing the conductivity of solutions of sodium benzoate made by the two methods. From the above results, it is seen that the titration method is sufficiently accurate.

$\mu_\infty$  for the sodium salts of all the toluic acids was deter-

mined in order to find out whether there is any difference in the migration velocities of isomeric ions. As there is no difference within the experimental error, the limiting conductivity for isomeric acids can be obtained from measurements on the sodium salt of any one of them. As  $\mu_{\infty}$  for the sodium salts of the dibasic acids cannot be experimentally determined, Ostwald's method for calculating this quantity was made use of. If the limiting conductivities of the sodium salts of the monobasic acids are plotted as ordinates against the number of the atoms in the molecule as abscissae, a fairly regular curve is obtained. From this curve  $\mu_{\infty}$  for the sodium salts of the dibasic acids may be read off. Even if the value calculated contains an appreciable error, the percentage error introduced into  $\mu_{\infty}$  of the organic acid itself will be much less.

The limiting conductivities of many of the organic acids worked with are given below,  $\mu_{\infty}$  for the dibasic acids being obtained as described in the preceding paragraph.

*Limiting Conductivities.*

Acid.	$\mu_{\infty}$ 0°.	$\mu_{\infty}$	$\mu_{\infty}$ 25°.	$\mu_{\infty}$ 35°.
Acetic	227	292 (12°)	361	412
Propionic	223	260 (6°.9)	354	405
Butyric	223	273 (9°.4)	354	404
Toluic	221	284 (12°.0)	349	397
Mandelic	221	283 (12°.0)	349	397
Hippuric	219	280 (12°.0)	345	392
Malonic	223	250 (4°.9)	355	405
Maleic	223	289 (12°.0)	353	402
Crotonic	222	286 (12°.0)	352	402
Racemic	222	286 (12°.0)	350	398
Pyrotartaric	221	290 (12°.0)	349	397
Citric	219	311 (18°.1)	345	392
Pyromucic	223	286 (12°.0)	355	405
Benzoic	222	304 (15°.8)	351	400
Phthalic	221	267 (8°.23)	349	397
Cinnamic	220	248 (5°.3)	348	396
Hydroxybenzoic	223	260 (6°.9)	353	403
Gallic	220	254 (6°.5)	348	396
Sulphanilic	222	255 (6°.3)	351	400
Aminobenzoic	221	260 (7°.5)	349	396

*Results.*—The results are tabulated in the following pages, molecular conductivities ( $\mu_v$ ) being expressed in Siemen's units. The temperature coefficients expressed in conductivity units and percentages need no explanation.

Table I.—Acetic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 9°.2.	$\mu_v$ 25°.	$\mu_v$ 35°.
2	1.270	1.560	2.089	2.359
8	2.656	3.292	4.342	4.948
32	5.328	6.612	8.699	9.912
128	10.48	13.04	17.11	19.46
512	20.45	25.40	33.24	37.75
1024	28.03	34.95	45.87	52.09
2048	39.05	48.65	63.00	70.89

Temperature Coefficients.

V.	0°-9°.2.		9°.2-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.49	0.03	2.15	0.03	1.30
8	0.07	2.61	0.07	2.02	0.06	1.40
32	0.14	2.62	0.13	2.00	0.12	1.39
128	0.28	2.66	0.26	1.98	0.24	1.37
512	0.54	2.63	0.50	1.96	0.45	1.36
1024	0.72	2.57	0.69	1.95	0.62	1.32
2048	1.04	2.67	0.91	1.87	0.79	1.25

Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 9°.2.	$\alpha$ 25°.	$\alpha$ 35°.
2	0.56	0.56	0.58	0.57
8	1.18	1.19	1.20	1.20
32	2.37	2.40	2.41	2.41
128	4.62	4.71	4.74	4.72
512	8.80	9.13	9.21	9.16
1024	12.35	12.51	12.71	12.64
2048	17.20	17.56	17.45	17.21

Dissociation Constants  $\times 10^4$ .

V.	0°.	9°.2.	25°.	35°.
2	0.157	0.159	0.169	0.165
8	0.175	0.179	0.183	0.182
32	0.179	0.184	0.186	0.185
128	0.175	0.182	0.184	0.183
512	0.166	0.179	0.182	0.181
1024	0.170	0.175	0.181	0.179
2048	0.174	0.179	0.180	0.175

Table II.—Propionic Acid.

*Molecular Conductivity.*

V.	$\mu_v$ 0°.	$\mu_v$ 6°.9.	$\mu_v$ 25°.	$\mu_v$ 35°.
2	1.030	1.217	1.700	1.913
8	2.291	2.700	3.704	4.207
32	4.631	5.450	7.436	8.422
128	9.004	10.60	14.57	16.50
512	17.47	20.59	28.40	32.14
1024	23.82	28.03	38.94	44.06
2048	32.43	39.24	53.47	60.28

*Temperature Coefficients.*

V.	0°–6°.9.		6°.9–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.63	0.03	2.19	0.02	1.25
8	0.06	2.59	0.06	2.05	0.05	1.36
32	0.12	2.56	0.11	2.01	0.10	1.33
128	0.23	2.58	0.22	2.07	0.19	1.32
512	0.45	2.59	0.43	2.10	0.37	1.32
1024	0.61	2.56	0.59	2.11	0.51	1.31
2048	0.84	2.52	0.79	2.01	0.68	1.27

*Percentage Dissociation.*

V.	$\alpha$ 0°.	$\alpha$ 6°.9.	$\alpha$ 25°.	$\alpha$ 35°.
2	0.46	0.47	0.48	0.47
8	1.03	1.04	1.05	1.04
32	2.08	2.10	2.10	2.08
128	4.04	4.08	4.12	4.07
512	7.83	7.92	8.02	7.93
1024	10.69	10.78	11.00	10.87
2048	14.99	15.09	15.10	14.88

*Dissociation Constants  $\times 10^4$ .*

V.	0°.	6°.9	25°.	35°.
2	0.107	0.111	0.116	0.112
8	0.133	0.136	0.138	0.137
32	0.138	0.140	0.141	0.138
128	0.133	0.135	0.138	0.135
512	0.130	0.133	0.137	0.134
1024	0.125	0.127	0.123	0.130
2048	0.129	0.131	0.131	0.127

Table III.—*n*-Butyric Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 9° 4.	$\mu_v$ 25°.	$\mu_v$ 35°.
2	1.090	1.341	1.730	1.930
8	2.501	3.062	3.891	4.351
32	5.072	6.230	7.902	8.801
128	10.00	12.23	15.45	17.14
512	19.44	23.79	29.86	33.00
1024	26.82	32.83	41.22	45.26
2048	37.37	45.63	89.20	62.71

## Temperature Coefficients.

V.	0°-9° 4.		9° 4-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.08	2.44	0.03	1.87	0.02	1.16
8	0.06	2.38	0.05	1.74	0.05	1.19
32	0.12	2.43	0.11	1.72	0.09	1.14
128	0.24	2.44	0.21	0.69	0.17	1.09
512	0.46	2.38	0.39	1.64	0.31	1.05
1024	0.64	2.38	0.54	1.64	0.40	0.98
2048	0.88	2.35	0.74	1.61	0.55	0.96

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 9° 4.	$\alpha$ 25°.	$\alpha$ 35°.
2	0.49	0.49	0.49	0.48
8	1.12	1.12	1.10	1.08
32	2.27	2.28	2.23	2.18
128	4.48	4.48	4.36	4.24
512	8.72	8.71	8.44	8.17
1024	12.02	12.02	11.64	11.20
2048	16.76	16.71	16.15	15.52

Dissociation Constants  $\times 10^4$ .

V.	0°.	9° 4.	25°.	35°.
2	0.120	0.120	0.120	0.115
8	0.159	0.159	0.153	0.147
32	0.165	0.166	0.157	0.152
128	0.164	0.164	0.152	0.147
512	0.163	0.163	0.152	0.142
1024	0.161	0.161	0.150	0.138
2048	0.165	0.164	0.152	0.139



Table IV.—Isobutyric Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 16°.46.	$\mu_v$ 25°.	$\mu_v$ 35°.
2	1.034	1.450	1.633	1.841
8	2.453	3.412	3.821	4.272
32	4.912	6.809	7.621	8.514
128	9.736	13.48	15.13	16.90
512	18.91	26.01	29.30	32.70
1024	26.32	36.18	40.90	45.54
2048	35.96	49.22	55.01	61.35

## Temperature Coefficients.

V.	0°–16°.46.		16°.46–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.03	2.45	0.02	1.48	0.02	1.27
8	0.06	2.38	0.05	1.40	0.05	1.18
32	0.12	2.35	0.10	1.40	0.09	1.17
128	0.23	2.33	0.19	1.43	0.18	1.17
512	0.43	2.28	0.36	1.41	0.34	1.16
1024	0.60	2.28	0.51	1.41	0.46	1.13
2048	0.81	2.24	0.68	1.38	0.63	1.15

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 16°.46.	$\alpha$ 25°.	$\alpha$ 35°.
2	0.47	0.47	0.46	0.46
8	1.10	1.10	1.08	1.06
32	2.20	2.20	2.15	2.11
128	4.37	4.35	4.27	4.18
512	8.48	8.39	8.28	8.09
1024	11.80	11.67	11.55	11.27
2048	16.13	15.88	15.54	15.19

 Dissociation Constants  $\times 10^4$ .

V.	0°.	16°.46.	25°.	35°.
2	0.108	0.110	0.108	0.108
8	0.153	0.153	0.147	0.141
32	0.155	0.154	0.148	0.142
128	0.156	0.154	0.149	0.143
512	0.154	0.150	0.146	0.139
1024	0.154	0.150	0.147	0.140
2048	0.151	0.146	0.140	0.133

Table V.—Phenylacetic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 13°.25.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	9.001	11.76	14.15	15.90
128	17.82	23.39	27.96	31.26
512	33.35	43.51	52.39	58.55
1024	45.68	59.59	71.63	79.84
2048	61.00	79.49	95.50	106.3

## Temperature Coefficients.

V.	0°–13°.25.		13°.25–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.21	2.32	0.20	1.73	0.18	1.23
128	0.41	2.32	0.40	1.70	0.33	1.18
512	0.77	2.30	0.76	1.72	0.62	1.18
1024	1.05	2.30	1.03	1.72	0.82	1.15
2048	1.40	2.29	1.36	1.71	1.06	1.13

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 13°.25.	$\alpha$ 25°.	$\alpha$ 35°.
32	4.07	4.06	4.05	4.01
128	8.06	8.06	8.01	7.87
512	15.09	15.01	14.97	14.75
1024	20.67	20.55	20.52	20.11
2048	27.60	27.41	27.36	26.77

Dissociation Constants  $\times 10^4$ .

V.	0°.	13°.25.	25°.	35°.
32	0.540	0.536	0.536	0.522
128	0.552	0.553	0.545	0.526
512	0.524	0.518	0.515	0.499
1024	0.526	0.519	0.518	0.494
2048	0.514	0.507	0.504	0.478

Table VI.—Mandelic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
8	12.60	16.10	19.86	22.45
32	24.49	31.21	38.56	43.62
128	46.40	59.64	72.96	82.39
512	82.21	106.1	129.6	146.2
1024	106.0	135.2	167.4	188.7
2048	132.4	168.3	205.5	234.5

## Temperature Coefficients.

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.29	2.32	0.29	1.80	0.26	1.30
32	0.56	2.29	0.56	1.81	0.51	1.31
128	1.10	2.38	1.02	1.72	0.94	1.29
512	1.99	2.42	1.81	1.71	1.66	1.28
1024	2.43	2.30	2.48	1.83	2.13	1.27
2048	2.99	2.26	2.86	1.70	2.90	1.40

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
8	5.70	5.69	5.69	5.65
32	11.09	11.03	11.05	10.98
128	20.99	20.78	20.90	20.75
512	37.20	36.98	37.15	36.84
1024	47.96	47.76	47.97	47.53
2048	59.91	59.47	59.03	59.06

 Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
8	4.32	4.29	4.29	4.24
32	4.30	4.27	4.29	4.24
128	4.36	4.26	4.31	4.25
512	4.30	4.24	4.30	4.20
1024	4.32	4.26	4.32	4.21
2048	4.37	4.26	4.16	4.16

Table VII.—*Hippuric Acid. Molecular Conductivity.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu$ 35°.
128	33.96	44.42	55.17	62.15
512	61.66	80.54	100.2	113.5
1024	81.10	105.8	131.1	147.2
2048	103.0	134.1	165.8	185.9

*Temperature Coefficients.*

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
128	0.87	2.57	0.83	1.86	0.70	1.27
512	1.57	2.55	1.52	1.84	1.25	1.25
1024	2.06	2.54	1.95	1.84	1.61	1.23
2048	2.59	2.52	2.44	1.82	2.01	1.21

*Percentage Dissociation.*

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
128	15.51	15.86	15.99	15.85
512	28.16	28.76	29.04	28.96
1024	37.03	37.79	38.00	37.55
2048	47.03	47.88	48.06	47.42

*Dissociation Constants  $\times 10^4$ .*

V.	0°.	12°.	25°.	35°.
128	2.22	2.34	2.38	2.33
512	2.16	2.27	2.32	2.31
1024	2.13	2.24	2.28	2.26
2048	2.04	2.15	2.17	2.09

Table VIII.—Malonic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 4° 9.	$\mu_v$ 25°.	$\mu_v$ 35°.
2	11.81	13.34	19.61	22.51
8	23.19	26.20	38.40	44.03
32	43.51	49.25	72.23	82.55
128	78.30	88.83	129.8	148.2
512	127.1	143.4	208.7	237.4
1024	153.3	173.2	251.2	284.8
2048	176.9	199.1	289.1	327.6

## Temperature Coefficients.

V.	0°–4° 9.		4° 9–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
2	0.31	2.64	0.31	2.34	0.29	1.48
8	0.61	2.66	0.61	2.32	0.58	1.47
32	1.17	2.69	1.14	2.32	1.03	1.43
128	2.09	2.67	2.04	2.30	1.84	1.42
512	3.33	2.62	3.25	2.27	2.87	1.38
1024	4.06	2.65	3.88	2.24	3.36	1.34
2048	4.53	2.56	4.48	2.25	3.75	1.30

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 4° 9.	$\alpha$ 25°.	$\alpha$ 35°.
2	5.30	5.34	5.53	5.55
8	10.40	10.48	10.81	10.87
32	19.57	19.70	20.34	20.38
128	35.12	35.53	36.58	36.59
512	56.99	57.36	58.80	58.60
1024	68.74	69.28	70.76	70.31
2048	79.32	79.66	81.45	80.89

 Dissociation Constants  $\times 10^4$ .

V.	0°.	4° 9.	25°.	35°.
2	14.8	15.0	16.1	16.4
8	15.1	15.3	16.4	16.5
32	14.8	15.1	16.3	16.3
128	14.8	15.3	16.4	16.5
512	14.8	15.1	16.4	16.2
1024	14.8	15.3	16.7	16.3
2048	14.9	15.3	17.5	16.8

Table IX.—Succinic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 5°.7.	$\mu_v$ 25°.	$\mu_v$ 35°.
8	4.570	5.371	8.032	9.251
32	9.211	10.72	16.01	18.36
128	18.24	21.35	31.24	35.80
512	34.75	40.59	59.34	67.87
1024	47.89	55.91	81.31	92.89
2048	64.61	75.29	109.6	124.8

## Temperature Coefficients.

V.	0°-5°.7.		5°.7-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.14	3.07	0.14	2.57	0.12	1.52
32	0.28	3.03	0.27	2.56	0.24	1.47
128	0.55	2.99	0.51	2.40	0.46	1.46
512	1.02	2.95	0.97	2.39	0.85	1.44
1024	1.41	2.94	1.32	2.36	1.16	1.42
2048	1.87	2.90	1.78	2.36	1.52	1.39

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 5°.7.	$\alpha$ 25°.	$\alpha$ 35°.
8	2.05	2.15	2.26	2.28
32	4.13	4.29	4.51	4.53
128	8.18	8.54	8.80	8.84
512	15.58	16.24	16.72	16.76
1024	20.47	22.37	22.91	22.91
2048	28.97	30.11	30.88	30.81

Dissociation Constants  $\times 10^4$ .

V.	0°.	5°.7.	25°.	35°.
8	0.537	0.590	0.655	0.667
32	0.556	0.600	0.666	0.673
128	0.569	0.623	0.664	0.670
512	0.562	0.615	0.655	0.659
1024	0.572	0.629	0.665	0.665
2048	0.577	0.634	0.675	0.670



Table X.—Maleic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	108.1	141.0	175.4	198.8
128	159.2	206.6	256.2	290.7
512	198.5	257.4	317.6	360.8
1024	212.8	274.7	337.9	384.6
2048	221.1	286.6	352.3	400.8

## Temperature Coefficients.

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	2.74	2.54	2.65	1.88	2.34	1.34
128	3.95	2.48	3.82	1.85	3.45	1.35
512	4.85	2.50	4.63	1.80	4.32	1.36
1024	5.14	2.43	4.86	1.77	4.67	1.38
2048	5.46	2.47	5.05	1.76	4.85	1.41

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
32	48.48	48.78	49.72	49.46
128	71.50	71.50	72.56	72.31
512	89.00	89.06	89.97	89.76
1024	95.06	95.06	95.72	95.68
2048	99.10	99.17	99.79	99.72

 Dissociation Constants  $\times 10^4$ .

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
32	143.0	145.0	154.0	151.0
128	141.0	140.0	150.0	148.0
512	141.0	142.0	158.0	154.0
1024	179.0	179.0	209.0	208.0
2048	...	...	...	...

Table XI.—Fumaric Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	35.46	46.66	58.00	65.79
128	65.67	86.42	107.2	121.2
512	114.1	149.1	184.9	209.6
1024	141.4	184.9	228.1	258.1
2048	176.5	229.0	281.0	318.1

## Temperature Coefficients.

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.94	2.64	0.87	1.87	1.78	1.19
128	1.73	2.63	1.60	1.85	1.46	1.20
512	2.92	2.56	2.75	1.85	2.47	1.18
1024	3.62	2.56	3.32	1.80	3.00	1.17
2048	4.33	2.45	4.00	1.75	3.71	1.17

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
32	15.90	16.14	16.43	16.37
128	29.45	29.90	30.37	30.15
512	51.17	51.59	52.37	52.14
1024	63.43	63.97	64.62	64.21
2048	79.14	79.23	79.60	79.12

Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
32	9.40	9.72	10.1	10.0
128	9.61	9.97	10.4	10.2
512	10.5	10.7	11.3	11.0
1024	10.7	11.1	11.5	11.2
2048	14.7	14.8	15.2	14.6

Table XII.—Citraconic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	68.66	85.82	103.0	115.1
128	114.3	144.0	173.4	194.4
512	165.9	210.2	255.4	288.2
1024	186.1	237.0	289.1	226.5
2048	200.5	257.1	315.0	356.0

## Temperature Coefficients.

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	1.43	2.08	1.32	1.54	1.21	1.18
128	2.48	2.17	2.26	1.57	2.10	1.21
512	3.69	2.23	3.48	1.65	3.28	1.28
1024	4.24	2.28	4.00	1.69	3.74	1.29
2048	4.70	2.34	4.46	1.74	4.10	1.30

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
32	31.02	30.16	29.34	28.77
128	51.64	50.60	49.40	48.60
512	74.98	73.86	72.76	72.04
1024	84.09	83.28	82.37	81.62
2048	90.59	90.31	89.74	89.01

 Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
32	43.6	40.7	38.1	36.3
128	43.1	40.5	37.7	35.9
512	43.9	40.8	38.0	36.2
1024	43.4	40.5	37.6	35.4
2048	42.6	41.0	38.3	35.3

Table XIII.—Mesaconic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	33.31	42.85	52.00	58.04
128	62.60	80.18	97.30	108.5
512	108.0	139.0	168.5	188.2
1024	134.7	172.9	209.8	234.0
2048	160.9	206.3	250.0	278.8

## Temperature Coefficients.

V.	0°-12°.		12°-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.80	2.39	0.70	1.63	0.60	1.16
128	1.47	2.36	1.32	1.64	1.12	1.15
512	2.54	2.35	2.27	1.63	1.97	1.16
1024	3.78	2.37	2.84	1.64	2.42	1.15
2048	4.09	2.35	3.36	1.63	2.88	1.15

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
32	15.05	15.04	14.81	14.51
128	28.29	28.17	27.72	27.13
512	48.79	48.67	48.00	47.06
1024	60.87	60.74	59.77	58.49
2048	72.69	72.49	71.22	69.69

Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
32	8.4	8.4	8.1	7.7
128	8.7	8.6	8.3	7.9
512	9.1	9.0	8.6	8.2
1024	9.3	9.2	8.7	8.1
2048	9.5	9.3	8.6	9.8

Table XIV.—Itaconic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 18°.12.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	13.50	20.77	23.68	27.22
128	26.00	39.95	45.52	52.21
512	49.51	74.57	84.74	97.11
1024	66.70	99.51	113.3	129.8
2048	87.91	129.9	147.3	167.5

## Temperature Coefficients.

V.	0°-18°.12.		18°.12-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.40	2.97	0.42	2.04	0.35	1.50
128	0.77	2.97	0.83	2.03	0.67	1.47
512	1.38	2.79	1.48	1.98	1.24	1.46
1024	1.81	2.71	2.01	2.01	1.65	1.45
2048	2.32	2.64	2.53	1.95	2.02	1.44

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 18°.12.	$\alpha$ 25°.	$\alpha$ 35°.
32	6.10	6.57	6.75	6.80
128	11.75	12.64	12.97	13.05
512	22.38	23.60	24.15	24.28
1024	30.14	31.49	32.28	32.45
2048	39.72	41.11	41.98	41.87

 Dissociation Constants  $\times 10^4$ .

V.	0°.	18°.12.	25°.	35°.
32	1.24	1.45	1.53	1.55
128	1.23	1.43	1.51	1.53
512	1.26	1.43	1.50	1.52
1024	1.27	1.42	1.50	1.52
2048	1.28	1.40	1.49	1.47

Table XV.—Crotonic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
8	2.752	3.640	4.550	5.177
32	5.526	7.312	9.123	10.31
128	10.92	14.49	18.00	20.29
512	21.25	28.23	35.15	39.85
1024	29.14	38.50	48.04	54.60
2048	39.78	53.41	65.33	74.19

## Temperature Coefficients.

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.07	2.69	0.07	1.92	0.06	1.38
32	0.15	2.69	0.14	1.91	0.12	1.31
128	0.30	2.72	0.27	1.86	0.23	1.27
512	0.58	2.74	0.53	1.89	0.47	1.34
1024	0.78	2.68	0.73	1.91	0.66	1.37
2048	1.05	2.67	0.99	1.90	0.89	1.36

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
8	1.24	1.27	1.29	1.29
32	2.49	2.56	2.59	2.57
128	4.92	5.07	5.11	5.05
512	9.57	9.87	10.00	9.91
1024	13.12	13.46	13.65	13.58
2048	17.74	18.32	18.57	18.45

Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
8	0.195	0.205	0.212	0.211
32	0.199	0.210	0.215	0.211
128	0.199	0.211	0.215	0.210
512	0.198	0.211	0.216	0.213
1024	0.194	0.205	0.211	0.208
2048	0.187	0.201	0.207	0.204



Table XVI.—*Racemic Acid. Molecular Conductivity.*

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
8	18.02	24.35	30.97	35.98
32	34.60	46.85	59.65	69.03
128	63.24	85.15	108.2	124.7
512	110.6	147.8	187.0	215.1
1024	139.0	183.7	230.0	264.3
2048	175.3	231.5	290.4	333.8

*Temperature Coefficients.*

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	1.53	2.93	0.51	2.09	0.50	1.62
32	1.02	2.93	0.99	2.10	0.95	1.59
128	1.83	2.89	1.77	2.08	1.65	1.53
512	3.10	2.80	3.02	2.04	2.81	1.50
1024	3.73	2.68	3.56	2.94	3.43	1.49
2048	4.68	2.67	4.53	1.95	4.34	1.50

*Percentage Dissociation.*

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
8	8.15	8.51	8.85	9.04
32	15.66	16.38	17.04	17.34
128	28.62	29.77	30.91	31.32
512	50.03	51.68	53.42	54.04
1024	62.90	64.22	65.70	66.40
2048	79.30	80.93	82.96	83.85

*Dissociation Constants  $\times 10^4$ .*

V.	0°.	12°.	25°.	35°.
8	9.1	9.9	10.8	11.2
32	9.1	10.0	10.9	11.3
128	9.0	9.9	10.8	11.2
512	9.8	10.8	12.0	12.4
1024	10.44	11.3	12.3	12.8
2048	14.8	16.8	19.7	21.3

Table XVII.—Pyrotartaric Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
8	5.403	7.150	9.045	10.41
32	10.94	14.41	18.13	20.80
128	21.08	27.68	35.00	40.00
512	40.45	53.06	67.02	76.56
1024	54.18	71.31	89.73	102.4
2048	73.00	96.00	120.3	137.7

## Temperature Coefficients.

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.15	2.70	0.15	2.04	0.14	1.49
32	0.29	2.64	0.29	1.99	0.27	1.47
128	0.56	2.61	0.56	2.03	0.50	1.43
512	1.05	2.60	1.07	2.02	0.95	1.42
1024	1.43	2.63	1.42	1.99	1.27	1.42
2048	1.92	2.62	1.87	1.95	1.74	1.45

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
8	2.44	2.46	2.59	2.62
32	4.95	4.97	5.20	5.24
128	9.54	9.55	10.03	10.08
512	18.30	18.30	19.21	19.29
1024	24.51	24.60	25.71	25.79
2048	33.03	33.11	34.46	34.69

Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
8	77	78	86	89
32	81	81	89	90
128	79	79	87	88
512	80	80	89	90
1024	78	78	87	88
2048	80	80	88	90

Table XVIII.—Citric Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 18°.10.	$\mu_v$ 25.	$\mu_v$ 35°.
8	15.64	24.34	27.50	32.05
32	30.27	46.74	52.76	61.42
128	55.94	86.40	97.30	112.7
512	97.22	148.3	167.6	195.1
1024	127.3	193.3	218.1	251.9
2048	153.2	229.3	257.9	297.8

## Temperature Coefficients.

V.	0°–18°.10.		18°.10–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.48	3.07	0.46	1.88	0.46	1.66
32	0.91	3.00	0.87	1.87	0.87	1.64
128	1.68	3.01	1.58	1.83	1.54	1.58
512	2.82	2.90	2.80	1.87	2.66	1.58
1024	3.64	2.86	3.59	1.86	3.38	1.55
2048	4.20	2.75	4.15	1.81	3.99	1.55

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 18°.10.	$\alpha$ 25°.	$\alpha$ 35°.
8	7.14	7.82	7.97	8.18
32	13.82	15.03	15.30	15.67
128	25.55	27.77	28.20	28.74
512	44.40	47.46	48.59	49.76
1024	58.13	62.16	63.23	64.25
2048	69.97	73.72	74.74	75.98

 Dissociation Constants  $\times 10^4$ .

V.	0°.	18°.10.	25°.	35°.
8	6.87	8.30	8.63	9.10
32	6.92	8.30	8.63	9.10
128	6.85	8.34	8.66	9.05
512	6.92	8.38	8.97	9.63
1024	7.88	9.96	10.6	11.3
2048	7.96	10.1	10.8	11.7

Table XIX.—Pyromucic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
8	17.47	22.01	26.29	28.94
32	34.24	42.76	51.15	56.37
128	62.90	79.22	94.61	104.5
512	107.1	136.4	163.2	108.0
1024	132.0	169.0	201.3	222.9
2048	159.5	203.0	245.1	270.1

## Temperature Coefficients.

V.	0°-12°.		12°-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
8	0.38	2.18	0.33	1.50	0.28	1.05
32	0.71	2.08	0.65	1.61	0.52	1.04
128	1.36	2.16	1.18	1.50	0.99	1.05
512	2.44	2.28	2.06	1.51	1.68	1.03
1024	3.08	2.31	2.49	1.47	2.06	1.02
2048	3.62	2.27	3.24	1.59	2.50	1.02

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
8	7.83	7.64	7.38	7.15
32	15.36	14.85	14.41	13.92
128	28.21	27.51	26.65	25.80
512	48.03	47.36	45.97	44.44
1024	59.20	58.68	56.99	55.03
2048	71.53	70.49	69.05	66.70

Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
8	8.3	7.9	7.4	6.9
32	8.7	8.1	7.6	7.0
128	8.7	8.1	7.6	7.0
512	8.7	8.3	7.6	6.9
1024	8.4	8.1	7.4	6.6
2048	8.7	8.2	7.5	6.5

Table XX.—Benzoic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 15°.80.	$\mu_v$ 25°.	$\mu_v$ 35°.
64	13.42	19.08	22.29	25.40
128	18.49	26.93	31.39	35.71
512	36.00	51.30	59.79	67.81
1024	47.63	68.33	79.56	90.11
2048	64.95	91.30	106.0	119.7

## Temperature Coefficients.

V.	0°–15°.80°.		15°.80–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.36	2.67	0.35	1.83	0.31	1.40
128	0.50	2.66	0.49	1.81	0.43	1.38
512	0.97	2.64	0.92	1.81	0.80	1.35
1024	1.26	2.64	1.22	1.79	1.06	1.33
2048	1.67	2.57	1.60	1.75	1.37	1.30

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 15°.80.	$\alpha$ 25°.	$\alpha$ 35°.
64	6.04	6.32	6.35	6.34
128	8.46	8.92	8.94	8.92
512	16.21	17.00	17.02	16.94
1024	21.45	22.62	22.67	22.52
2048	29.25	30.24	30.20	29.92

 Dissociation Constants  $\times 10^4$ .

V.	0°.	15°.80	25°.	35°.
64	0.607	0.666	0.672	0.672
128	0.611	0.682	0.686	0.684
512	0.613	0.679	0.683	0.676
1024	0.572	0.646	0.649	0.640
2048	0.591	0.640	0.638	0.624

Table XXI.—o-Toluic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
512	54.71	68.32	81.09	88.44
1024	71.65	89.87	106.7	116.7
2048	95.06	118.7	141.0	154.7

## Temperature Coefficients.

V.	0°-12°.		12°-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	1.13	2.07	0.98	1.44	0.74	0.91
1024	1.52	2.11	1.29	1.44	1.00	0.94
2048	1.93	2.03	1.72	1.44	1.33	0.94

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
512	24.76	24.11	23.23	22.20
1024	32.44	31.71	30.50	29.47
2048	43.01	41.75	40.54	39.16

Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
512	1.59	1.49	1.37	1.25
1024	1.52	1.44	1.32	1.30
2048	1.59	1.46	1.35	1.22



Table XXII.—*m*-Toluic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
512	33.05	43.57	54.60	62.05
1024	45.20°	59.43	74.16	83.93
2048	61.24	80.79	100.4	113.1

## Temperature Coefficients.

V	0°-12°.		12°-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	0.88	2.65	0.85	1.95	0.75	1.37
1024	1.19	2.62	1.13	1.91	0.98	1.32
2048	1.63	2.66	1.51	1.87	1.27	1.27

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
512	14.95	15.44	15.64	15.63
1024	20.45	21.05	21.25	21.14
2048	27.71	28.63	28.77	28.49

 Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
512	0.513	0.550	0.567	0.565
1024	0.513	0.548	0.560	0.554
2048	0.519	0.560	0.567	0.554

Table XXIII.—p-Toluic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
512	...	...	48.48	55.44
1024	39.63	52.52	66.13	75.54
2048	54.12	71.75	89.96	103.5

## Temperature Coefficients.

V.	0°-12°.		12°-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	....	....	....	....	0.70	1.44
1024	1.07	2.76	1.05	1.99	0.94	1.42
2048	1.47	2.72	1.40	1.95	1.35	1.50

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
512	...	...	13.89	13.96
1024	17.93	18.49	18.95	19.02
2048	24.49	25.26	25.78	26.07

Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
512	...	...	0.438	0.433
1024	0.383	0.410	0.433	0.437
2048	0.388	0.417	0.437	0.449

Table XXIV.—o-Phthalic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 8°.23.	$\mu_v$ 25°.	$\mu_v$ 35°.
64	55.98	66.45	85.92	96.48
128	75.56	88.32	114.8	128.9
512	122.3	145.7	189.2	212.5
1024	148.2	177.1	231.9	259.7
2048	174.2	208.4	272.7	306.0

## Temperature Coefficients.

V.	0°-8°.23.		8°.23-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	1.27	2.27	1.16	1.75	1.06	1.23
128	1.67	2.24	1.58	1.79	1.41	1.23
512	2.84	2.33	2.59	1.78	2.33	1.23
1024	3.51	2.37	3.27	1.85	2.78	1.20
2048	4.16	2.39	3.83	1.84	3.33	1.22

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 8°.23.	$\alpha$ 25°.	$\alpha$ 35°.
64	25.33	24.89	24.62	24.31
128	33.75	33.09	32.90	32.47
512	55.34	54.58	54.23	53.52
1024	67.07	66.33	66.45	65.42
2048	78.81	78.05	78.14	77.07

 Dissociation Constants  $\times 10^4$ .

V.	0°.	8°.23.	25°.	35°.
64	13.4	12.9	12.6	12.2
128	13.4	12.8	12.6	12.2
512	13.4	12.8	12.5	12.0
1024	13.4	12.8	12.8	12.1
2048	14.3	13.6	13.6	12.7

Table XXV.—Cinnamic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 5°.3.	$\mu_v$ 25°.	$\mu_v$ 35°.
512	26.50	30.67	44.60	50.70
1024	36.40	42.11	61.22	69.63
2048	49.69	57.40	83.45	94.81

Temperature Coefficients.

V.	0°–5°.3.		5°.3–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
512	0.79	2.97	0.71	2.31	0.61	1.37
1024	1.08	2.96	0.97	2.30	0.84	1.37
2048	1.46	2.93	1.32	2.30	1.14	1.36

Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 5°.3.	$\alpha$ 25°.	$\alpha$ 35°.
512	12.04	12.37	12.81	12.80
1024	16.55	16.97	17.59	17.58
2048	22.08	23.14	23.98	23.94

Dissociation Constants  $\times 10^4$ .

V.	0°.	5°.3	25°.	35°.
512	0.322	0.341	0.368	0.367
1024	0.320	0.339	0.367	0.366
2048	0.305	0.342	0.370	0.368

Table XXVI.—Salicylic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 6°.9.	$\mu_v$ 25°.	$\mu_v$ 35°.
64	...	...	80.50	92.80
128	62.65	75.59	108.3	125.1
512	105.4	126.4	181.2	207.0
1024	130.7	156.9	223.2	255.4
2048	153.8	183.9	259.9	295.7

## Temperature Coefficients.

V.	0°-6°.9.		6°.9-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	....	....	....	....	1.23	1.53
128	1.88	2.99	1.83	2.42	1.68	1.55
512	3.12	2.96	3.00	2.37	2.58	1.42
1024	3.80	2.91	3.63	2.31	3.22	1.41
2048	4.36	2.84	2.16	2.26	3.58	1.38

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 6°.9.	$\alpha$ 25°.	$\alpha$ 35°.
64	...	...	22.80	23.02
128	28.09	29.06	30.68	31.03
512	47.28	48.62	51.34	51.37
1024	58.60	60.34	63.22	63.37
2048	68.96	70.73	73.62	73.36

 Dissociation Constants  $\times 10^4$ .

V.	0°.	6°.9.	25°.	35°.
64	...	...	10.5	10.7
128	8.6	9.3	10.6	10.9
512	8.3	9.0	10.6	10.6
1024	8.1	9.0	10.6	10.7
2048	7.5	8.4	9.4	9.9

Table XXVII.—*m*-Hydroxybenzoic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 13°.22.	$\mu_v$ 25°.	$\mu_v$ 35°.
64	14.65	19.97	24.35	27.74
128	20.48	27.85	33.95	38.63
512	39.04	52.89	64.50	73.28
1024	53.09	72.01	87.80	99.70
2048	71.20	96.03	116.9	132.6

## Temperature Coefficients.

V.	0°-13°.22.		13°.22-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.40	2.75	0.37	1.86	0.34	0.39
128	0.56	2.72	0.52	1.86	0.47	1.38
512	1.05	2.68	0.99	1.86	0.88	1.36
1024	1.44	2.71	1.31	1.81	1.19	1.36
2048	1.94	2.74	1.72	1.78	1.57	1.34

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 13°.22.	$\alpha$ 25°.	$\alpha$ 35°.
64	6.57	6.82	6.90	6.88
128	9.18	9.50	9.62	9.58
512	17.51	18.05	18.27	18.19
1024	23.81	24.56	24.87	24.74
2048	31.93	32.77	33.12	32.91

Dissociation Constants  $\times 10^4$ .

V.	0°.	13°.22.	25°.	35°.
64	0.722	0.779	0.799	0.795
128	0.725	0.780	0.799	0.794
512	0.725	0.776	0.798	0.798
1024	0.726	0.781	0.804	0.794
2048	0.715	0.780	0.801	0.788



Table XXVIII.—p-Hydroxybenzoic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 13°.23.	$\mu_v$ 25.°	$\mu_v$ 35°.
64	8.746	11.99	14.79	16.97
128	18.29	16.81	20.69	23.71
512	23.87	32.45	39.96	45.77
1024	33.03	44.91	55.30	63.24
2048	44.40	60.39	74.14	85.60

## Temperature Coefficients.

V.	0°–13°.23.		13°.23–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.25	2.80	0.24	1.98	0.22	1.46
128	0.34	2.78	0.33	1.96	0.30	1.46
512	0.65	2.72	0.64	1.97	0.58	1.45
1024	0.90	2.72	0.88	1.97	0.79	1.44
2048	1.21	2.72	1.17	1.94	1.05	1.41

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 13°.23.	$\alpha$ 25°.	$\alpha$ 35°.
64	3.92	4.09	4.19	4.21
128	5.51	5.74	5.86	5.88
512	10.70	11.08	11.32	11.36
1024	14.81	15.32	15.66	15.70
2048	19.91	20.61	21.00	21.00

 Dissociation Constants  $\times 10^4$ .

V.	0°.	13°.23.	25°.	35°.
64	0.250	0.273	0.286	0.289
128	0.251	0.273	0.285	0.287
512	0.251	0.269	0.282	0.284
1024	0.252	0.271	0.284	0.285
2048	0.242	0.261	0.273	0.273

Table XXIX.—Gallic Acid. Molecular Conductivity.

V.	$\mu_{90}$ 0°.	$\mu_{90}$ 6°.5.	$\mu_{90}$ 25°.	$\mu_{90}$ 35°.
64	9.790	11.66	16.90	19.36
128	14.01	16.55	23.60	27.10
512	28.89	34.08	48.33	55.12
1024	37.84	44.63	62.50	71.18
2048	51.50	60.72	85.02	96.7

## Temperature Coefficients.

V.	0°-6°.5.		6°.5-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.29	2.94	0.28	2.43	0.25	1.46
128	0.39	2.79	0.38	2.30	0.35	1.48
512	0.80	2.77	0.77	2.26	0.68	1.41
1024	1.05	2.76	0.97	2.17	0.87	1.39
2048	1.42	2.75	1.31	2.16	1.17	1.38

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 6°.5.	$\alpha$ 25°.	$\alpha$ 35°.
64	4.44	4.59	4.86	4.89
128	6.36	6.51	6.78	6.85
512	13.11	13.41	13.89	13.92
1024	17.18	17.55	17.96	17.98
2048	23.37	23.88	24.43	24.43

Dissociation Constants  $\times 10^4$ .

V.	0°.	6°.5.	25°.	35°.
64	0.323	0.345	0.387	0.393
128	0.338	0.354	0.385	0.394
512	0.387	0.405	0.437	0.440
1024	0.348	0.365	0.384	0.385
2048	0.349	0.366	0.386	0.386

Table XXX.—Metanilic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 12°.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	11.60	18.01	26.89	35.01
128	22.90	34.84	51.40	66.89
512	42.76	65.66	95.10	121.1
1024	58.01	87.96	125.8	158.1
2048	76.38	115.1	162.8	203.5

## Temperature Coefficients.

V.	0°–12°.		12°–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.53	4.61	0.68	3.79	0.81	3.02
128	1.00	4.40	1.28	3.66	1.55	3.01
512	1.91	4.46	2.27	3.45	2.60	2.73
1024	2.50	2.30	2.91	3.41	3.23	2.63
2048	3.23	4.22	3.67	3.19	4.07	2.50

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 12°.	$\alpha$ 25°.	$\alpha$ 35°.
32	5.23	6.32	7.67	8.75
128	10.27	12.23	14.64	16.72
512	19.26	23.04	27.10	30.27
1024	26.13	30.87	25.84	39.53
2048	34.41	40.39	46.37	50.88

 Dissociation Constants  $\times 10^4$ .

V.	0°.	12°.	25°.	35°.
32	0.90	1.33	1.99	2.62
128	0.89	1.33	1.96	2.62
512	0.90	1.35	1.97	2.57
1024	0.90	1.35	1.96	2.52
2048	0.88	1.34	1.96	2.57

Table XXXI.—Sulphanilic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 6°.3.	$\mu_v$ 25°.	$\mu_v$ 35°.
32	21.80	27.25	47.20	60.0
128	40.66	50.89	87.51	110.2
512	74.25	91.33	152.8	188.3
1024	96.40	118.1	193.0	237.0
2048	121.5	148.4	235.2	281.5

## Temperature Coefficients.

V.	0°–6°.3.		6°.3–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
32	0.88	4.03	1.07	3.91	1.28	2.71
128	1.62	3.99	1.96	3.85	2.27	2.59
512	2.71	3.65	3.29	3.60	3.55	2.33
1024	3.45	3.57	4.01	3.39	4.40	2.28
2048	4.27	3.52	4.53	3.06	4.63	1.97

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 6°.3	$\alpha$ 25°.	$\alpha$ 35°.
32	9.82	10.69	13.45	15.00
128	18.31	19.96	24.93	27.55
512	33.44	35.82	43.52	47.08
1024	43.42	46.33	54.99	58.75
2048	54.71	58.21	67.02	70.37

Dissociation Constants  $\times 10^4$ .

V.	0°.	6°.3.	25°.	35°.
32	3.34	4.00	6.53	8.27
128	3.20	3.89	6.47	8.19
512	3.28	3.90	6.55	8.18
1024	3.26	3.90	6.56	8.17
2048	3.23	3.96	6.64	8.16

Table XXXII.—o-Aminobenzoic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 7°.5.	$\mu_v$ 25°.	$\mu_v$ 35°.
64	3.071	4.172	7.150	9.001
128	4.642	6.283	10.71	13.39
512	10.90	14.31	23.26	28.96
1024	16.03	20.48	33.53	41.57
2048	21.93	28.30	45.26	55.78

## Temperature Coefficients.

V.	0°-7°.5.		7°.5-25°.		25°-35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.15	4.78	0.17	4.08	0.19	2.59
128	0.21	4.52	0.25	3.98	0.27	2.57
512	0.45	4.17	0.51	3.58	0.57	2.45
1024	0.65	4.03	0.72	3.46	0.81	2.40
2048	0.85	3.87	0.97	3.43	1.05	2.33

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 7°.5.	$\alpha$ 25°.	$\alpha$ 35°.
64	1.39	1.60	2.05	2.27
128	2.12	2.42	3.07	3.38
512	4.93	5.50	6.67	7.31
1024	7.25	7.87	9.62	10.48
2048	7.88	10.88	13.00	14.07

 Dissociation Constants  $\times 10^4$ .

V.	0°.	7°.5.	25°.	35°.
64	0.0306	0.0408	0.0671	0.0824
128	0.0360	0.0467	0.0761	0.0922
512	0.0499	0.0626	0.0932	0.112
1024	0.0554	0.0658	0.100	0.120
2048	0.0329	0.0649	0.0948	0.113

Table XXXIII.—*p*-Aminobenzoic Acid. Molecular Conductivity.

V.	$\mu_v$ 0°.	$\mu_v$ 10°. 19.	$\mu_v$ 25°.	$\mu_v$ 35°.
64	3.711	5.136	7.370	8.919
128	5.346	7.527	10.84	12.97
512	12.57	17.39	24.54	29.06
1024	18.87	25.71	35.07	41.31
2048	28.32	37.21	50.13	58.56

## Temperature Coefficients.

V.	0°–10°. 19.		10°. 19–25°.		25°–35°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.	Cond. units.	Per cent.
64	0.14	3.78	0.15	2.92	0.16	2.10
128	0.21	4.00	0.22	2.97	0.21	1.96
512	0.47	3.76	0.48	2.78	0.45	1.84
1024	0.67	3.57	0.63	2.46	0.62	1.79
2048	0.87	3.08	0.87	2.35	0.84	1.68

## Percentage Dissociation.

V.	$\alpha$ 0°.	$\alpha$ 10°. 19.	$\alpha$ 25°.	$\alpha$ 35°.
64	1.68	1.87	2.11	2.25
128	2.42	2.75	3.11	3.27
512	5.69	6.34	7.04	7.47
1024	8.54	9.38	10.07	10.42
2048	13.73	13.28	14.38	14.77

Dissociation Constants  $\times 10^4$ .

V.	0°.	10°. 19.	25°.	35°.
64	0.0448	0.0559	0.0714	0.0790
128	0.0468	0.0606	0.0780	0.0865
512	0.0670	0.0838	0.104	0.118
1024	0.0678	0.0949	0.110	0.119
2048	0.107	0.104	0.118	0.125

While inorganic salts and mineral acids all behave in the same way with respect to the change in dissociation with the temperature, the organic acids present a perplexing problem, when an attempt is made to deduce any relation between the change in their dissociation and their chemical constitution. With many of the acids a maximum in dissociation occurs between 25° and 35°. This statement applies to the following acids: acetic, propionic, phenylacetic, hippuric, malonic, maleic, fumaric, crotonic, benzoic, *m*-toluic, cinnamic, salicylic, *m*-hydroxybenzoic. The dissociation of succinic, itaconic, racemic, pyrotartaric, citric, *p*-hydroxybenzoic, gallic,



metanilic, sulphanilic, *o*- and *p*-aminobenzoic acids, increases from 0° up to 35° without a maximum, but several give indications that a maximum would appear at a slightly higher temperature. The dissociation of the remaining acids—*n*-butyric and isobutyric, mandelic, citraconic, mesaconic, *o*-toluic, *o*-phthalic—decreases regularly with rise in temperature from 0°. The most probable dissociation constants of all the acids are given in Table XXXIV, from which the above relations become clear:

 Table XXXIV.— $K \times 10^4$ .

Acid.	0°.	12°.	25°.	35°.
Acetic	0.175	....	0.184	0.183
Propionic	0.133	....	0.138	0.136
<i>n</i> -Butyric	0.163	....	0.153	0.147
Isobutyric	0.155	....	0.148	0.142
Phenylacetic	0.540	....	0.545	0.526
Mandelic	4.30	4.29	4.29	4.24
Hippuric	2.22	2.34	2.38	2.33
Malonic	1.48	....	16.3	16.3
Succinic	0.562	....	0.655	0.659
Maleic	143.0	145.0	154.0	151.0
Fumaric	9.40	9.72	10.1	10.0
Citraconic	43.6	40.7	38.1	36.3
Mesaconic	8.4	8.4	8.1	7.7
Itaconic	1.24	1.45	1.53	1.55
Crotonic	0.199	0.210	0.215	0.211
Racemic	9.1	9.9	10.8	11.2
Pyrotartaric	79.0	79.0	87.0	88.0
Citric	6.85	....	8.66	9.05
Pyromucic	8.7	8.1	7.6	7.0
Benzoic	0.611	....	0.686	0.684
<i>o</i> -Toluic	1.59	1.49	1.37	1.25
<i>m</i> -Toluic	0.515	0.548	0.560	0.554
<i>p</i> -Toluic	0.383	0.410	0.433	0.437
<i>o</i> -Phthalic	13.4	....	12.6	12.2
Cinnamic	0.322	....	0.368	0.367
Salicylic	8.3	....	10.6	10.6
<i>m</i> -Hydroxybenzoic	0.725	....	0.798	0.789
<i>p</i> -Hydroxybenzoic	0.251	....	0.285	0.287
Gallic	0.338	....	0.385	0.394
Metanilic	0.90	1.33	1.99	2.62
Sulphanilic	3.28	....	6.55	8.18
<i>o</i> -Aminobenzoic	0.0306	....	0.0671	0.0824
<i>p</i> -Aminobenzoic	0.0448	....	0.0714	0.0790

The results obtained agree generally with those of Euler<sup>1</sup> and Schaller.<sup>2</sup> The former investigator, working at temperatures ranging from 0° to 50°, found that the dissociation of benzoic acid reached a maximum at 35°, while that of *m*-hydroxybenzoic attained a maximum between 25° and 35°. The dissociation of salicylic acid increased from 0° to 50°, while that of *o*-toluic acid decreased from 0°. Schaller, working at temperatures between 25° and 100°, found maxima in dissociation between 25° and 40° for cinnamic, benzoic, salicylic, *m*- and *p*-toluic acids, and observed, as the work of Euler and the results here recorded show, that the dissociation of *o*-toluic acid decreased with rise in temperature from the lowest temperature at which it was measured.

The hypothesis of Thomson<sup>3</sup> and Nernst,<sup>4</sup> which states that solvents having the greatest dissociating power have the largest dielectric constants, explains why the dissociation of inorganic salts and mineral acids decreases with rise in temperature, since it has been shown<sup>5</sup> that the dielectric constant of water decreases also with rise in temperature. Since maxima in dissociation have been found with many of the organic acids, other unknown forces must come into play in such cases. It is particularly interesting to note that such isomers as the toluic acids differ markedly with respect to the change of their dissociation with change in temperature.

#### SUMMARY OF FACTS ESTABLISHED.

1. The percentage temperature coefficients of conductivity of the organic acids are generally small and of the same order of magnitude, and decrease with rise in temperature and with increase in dilution. The coefficients expressed in conductivity units decrease with rise in temperature. These facts suggest that the acids are much less hydrated than the mineral acids, for reasons previously given.

2. The percentage coefficients of conductivity of the amino acids are exceptionally large, and the coefficients expressed

<sup>1</sup> Z. physik. Chem., **21**, 247 (1896).

<sup>2</sup> *Ibid.*, **25**, 497 (1898).

<sup>3</sup> Phil. Mag., **36**, 320 (1894).

<sup>4</sup> Z. physik. Chem., **13**, 531 (1894).

<sup>5</sup> Phil. Mag., [6] **7**, 655 (1904).

in conductivity units increase with rise in temperature. The internal salt-forming power of these amphoteric electrolytes explains such behavior.

3. The conductivity of most of the organic acids is a parabolic function of the temperature, as proved by comparing observed values with those calculated from interpolation formulae.

4. Several of the amino acids are again exceptions, and their conductivity is not a parabolic function of the temperature, for the same reasons which explain their large temperature coefficients.

5. There is no general statement possible concerning the change in dissociation of the organic acids with change in temperature. Maxima occur with several between  $25^{\circ}$  and  $35^{\circ}$ , while in other cases maxima are indicated at slightly higher temperatures than those at which measurements were made. The dissociation of several acids decreases regularly from  $0^{\circ}$ .

6. Isomeric acids do not behave similarly as regards change in their dissociation.

7. The migration velocities of isomeric ions are identical.

8. The behavior of the organic acids with respect to the change in their dissociation with the temperature is not in accord with the hypothesis of Thomson and Nernst, which connects dissociating power and dielectric constants; or at least the influence of some other unknown force is suggested.

This work will be extended for the organic acids from  $35^{\circ}$  to  $65^{\circ}$ , and also to nonaqueous solvents.

JOHNS HOPKINS UNIVERSITY,  
June, 1910.

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## REVIEWS.

QUANTITATIVE CHEMICAL ANALYSIS. Adapted for Use in the Laboratories of Schools and Colleges. By FRANK CLOWES, D.Sc., Lond., Emeritus Professor of Chemistry in the University College, Nottingham, and J. BERNARD COLEMAN, A.R.C.Sc., Dublin, Head of the Chemical Department in the Southwestern Polytechnic, Chelsea, S. W. Eighth Edition. Philadelphia: P. Blakiston's Son & Co. 1909. pp. xxiv + 565. Price, \$3.50.

The sixth edition of this well-known work has already been reviewed at some length in *THIS JOURNAL*.<sup>1</sup> In the present

<sup>1</sup> Vol. 31, p. 299.

edition the type has been entirely reset, and considerable addition has been made to the text and illustrative cuts. The size of the page has been increased somewhat, while the thickness of the book remains about as before.

According to the authors, the new matter introduced is as follows: a description of improved water stills and steam ovens; additional methods for the determination of melting and boiling points, for the electrolytic estimation of metals, for the volumetric estimation of hydrogen peroxide, formaldehyde, silver, tin and antimony alloys, for the estimation of preservatives in milk and butter, resin acids in soap, and poisonous metals and dissolved oxygen in water; also additional processes for the valuation of the ores of chromium, tin, arsenic, mercury and zinc, of soap by a shortened scheme, of burnt lime, mortar, cement, white metal, and the description and use of the bomb calorimeter for coal valuation.

A new section has been introduced on the examination of oils, fats and waxes, and a table of the constants and characteristics of the ordinary members of this class of substances has been inserted by means of which the results of the examination may be interpreted.

The book is an excellent compilation of analytical methods and will, doubtless, prove very useful to both the chemist and the student; it is open to question, however, whether a total disregard of the modern theories of solution in quantitative analysis is justifiable from the standpoint of teaching.

E. B. SPEAR.

A MANUAL OF QUALITATIVE ANALYSIS. By J. E. MCGREGORY. Professor of Chemistry and Mineralogy in Colgate University. Revised Edition. Boston: Ginn & Co. 1909. pp. xiv + 135. Price, \$1.00.

The first edition of this book, published in 1903, was reviewed in *THIS JOURNAL*.<sup>1</sup> The present edition is but little changed. It is thorough, carefully written and well arranged; it does not introduce modern theoretical or analytical methods. It may be recommended to the numerous teachers who prefer this type of book.

E. R.

AN INTRODUCTION TO CHEMICAL ANALYSIS, for Students of Medicine, Pharmacy, and Dentistry. By ELBERT W. ROCKWOOD, M.D., Professor of Chemistry and Toxicology and Head of the Department of Chemistry in the University of Iowa. Third Revised Edition. Philadelphia: P. Blakiston's Son & Co. 1909. Price, \$1.50.

The first edition of the book appeared in 1902<sup>2</sup> and the second in 1905.<sup>3</sup> Although it contains only 240 pages, it em-

<sup>1</sup> Vol. 31, p. 586.

<sup>2</sup> *THIS JOURNAL*, 27, 235.

<sup>3</sup> *Ibid.*, 34, 472.

braces qualitative analysis, volumetric analysis, the sanitary examination of water, the detection of poisons, analysis by the blowpipe, and the testing of reagents. Considerable attention is paid to the theory of electrolytic dissociation as a means of explaining the chemical reactions used in analytical chemistry, and this is, in the main, satisfactory, although the definition of solubility product is merely that it is "the product of the concentrations of the ions," and the fact that this is only true of a saturated solution is not made clear.

As a whole, the text is well written, although there is some evidence of careless statements. Thus the treatment recommended for insoluble tin oxide, and insoluble salts of lead and silver, is fusion with sodium carbonate on platinum. Again, in the detection of poisons, the author wisely points out the necessity of testing hydrochloric acid for arsenic, but forgets, in describing the test, that arsenic trichloride will distil off in concentrating a liter of acid to a volume of 20 cubic centimeters.

WILLIAM T. HALL.

FOOD INSPECTION AND ANALYSIS, for the Use of Public Analysts, Health Officers, Sanitary Chemists and Food Economists. By ALBERT E. LEACH, S.B., Chief of the Denver Food and Drug Inspection Laboratory, Bureau of Chemistry, U. S. Department of Agriculture. Second Edition, Revised and Enlarged. 40 full-page, half-tone plates. New York: Wiley and Sons; London: Chapman & Hall, Ltd. 1909. pp. xviii + 954. Price, \$7.50.

The first edition of this work was published in 1904. But few American chemists were then giving special attention to the examination of foods. The Association of Official Agricultural Chemists had just published its first compilation of food methods, representing the beginning of the system of cooperation and collaboration among American food chemists which has characterized their more recent work. Material progress had already been made by the Association of Official Agricultural Chemists in determining proper standards of composition of foods, and the foundation had been laid for the broader subsequent work on the same subject by the committee appointed jointly by the Association of Official Agricultural Chemists and the Association of State and National Dairy and Food Departments.

The first edition of this work, therefore, was written early in the present period of activity and immediately took the first rank among books of its class. It is universally considered indispensable in every food laboratory.

The second edition is cast on the same lines as the first but is a complete revision and brought thoroughly up to date. Almost every page is materially altered. Many of



the methods of analysis given in the first edition and since found unreliable have been replaced by others. The new methods introduced cover a wide variety of subjects: "Notable among these are meats and meat extracts, flour (including methods for determining the grade and for the detection of bleaching), noodles and Italian pastes, paprika, prepared mustard, tea, coffee, cocoa products (including milk chocolate), ice cream, maple products, honey, oils (including the Polenske number and Bömer's phytosterol-acetate test for vegetable oils), distilled liquors, preservatives (notably benzoic acid), etc.

"A separate chapter on the refractometer, its varieties and application to food analysis has been introduced; also a separate chapter on flavoring extracts, including the lesser used extracts of almond, peppermint, wintergreen, rose, cassia, and cloves."

In its second edition, the book is brought up to date and in many portions—notably in Chapters 10, 13, 14 and 15—it has been greatly strengthened. The preface gives to Dr. A. L. Winton credit for the greater portion of the work of revision, as the author was not at that time able to undertake it alone. It brings to us, therefore, the judgment and experience of two of the foremost food chemists.

The book is peculiarly a laboratory manual and is intended for the analyst alone. The work of the inspector is discussed only with reference to his relation to the analyst, while the subject of the prosecution of court cases is dismissed with a brief discussion of the testimony of analysts and with the statement that Massachusetts has found legal counsel superfluous in the trial of food cases in the lower courts.

It is the belief of the reviewer that the last statement is not applicable to the enforcement of the federal law or the laws of the majority of the states, especially in the trial of wealthy defendants who are represented by able counsel.

W. D. BIGELOW.

CHIMICA GENERALE E APPLICATA ALL'INDUSTRIA. Vol. II. Chimica Organica. DR. ETTORE MOLINARI. Milano: Ulrico Hoepli. 1908. pp. 980.

The multiplication of comprehensive and standard works on special branches of chemistry in all languages is a notable sign of the flourishing condition of this science. The present work in Italian is fully comparable with the best works on chemical technology such as we usually owe to the thoroughness of German chemists and the enterprise of German publishers. It is in no sense an imitation of one of these but



combines originality of subject matter with an excellent summary of organic chemistry as applied to the arts. The theoretical part, while necessarily brief, is clear and well compiled; a good feature is the number of tables of physical properties of homologues and isomers. As an illustration of the inclusive character of the technical portion may be cited articles on theories of the origin of petroleum, oxydases, alcoholism and its sociological influence, velocity of propagation of explosions, safe explosives for dangerous mines, destruction of explosives, saponification of fats by biological means (lipolytic enzymes), synthesis of alkaloids, artificial silk, etc. The book is to be highly recommended to those who read Italian.

B. B. TURNER.

BEET-SUGAR MAKING AND ITS CHEMICAL CONTROL. By Y. NIKAIDO. Easton, Pa.: The Chemical Publishing Co.

To quote from the preface: "The aim of this work is to aid those who are starting their career in the beet-sugar manufacture but lack systematic training in the technique thereof. Having this in view, the author has endeavored to explain not only the practical operations of sugarhouse stations but also the fundamental principles involved in the various processes of the sugarhouse and in the methods of analysis of various sugarhouse products."

In his endeavor to accomplish his purpose as outlined above, the author has condensed, in some two hundred and ninety odd pages, text covering the chemistry of the industry, inorganic and technical, as well as detailing processes and analytical methods and discussing the optics of the polariscope. The book shows much painstaking compilation and the subject matter is logically arranged, but aside from directions for analytical methods and description of processes and apparatus with which the author shows familiarity, the text is little more than a collection of notes such as any bright student might elaborate from his lecture courses. Great condensation is of course necessary for covering such an extensive field and that the quality of the text would be somewhat uneven is also obvious.

To the young chemist entering on his industrial career, who, as a rule, is continually looking for the book which will tell him all things necessary to know, Mr. Nikaido's work will be attractive, and perhaps even if the novice fails in getting a working knowledge of much that is presented, the book may prove the inspiration needed for more extended study. To the experienced man the book will be useful for handy reference.

The descriptions of apparatus and manipulation directions are clear and aided by numerous illustrations, although there is practically nothing on that useful and often abused instrument, the balance.

A commendable feature of the book is Table IV, an elaborate work arranged in an original manner, and comprising thirty-six pages of the appendix, which gives values for sucrose and purity for all sugarhouse liquors between  $7^{\circ}.1$  and  $27^{\circ}$  Brix for each tenth. By an ingenious adaptation of Weisberg's dilution method, the same table can be used for masse-cuites and molasses. It should be stated, however, that such tables, although used in one form or another almost universally in refinery practice, are only correct when polarizations are made at the standard Brix temperature. An analysis of the formula on which such tables are collected will show that the density should always be taken at *temperature of polarization* for calculating sucrose, the Brix reading, of course, being calculated for standard temperature. (The reviewer confesses that he has not been clear on this point in his own book, by the way.) The error at maximum room temperatures is but a few tenths of a per cent. and can be shown experimentally by comparing results with those obtained by using an accurate sucrose pipette or by polarizing the normal weight of solution. Hence it is negligible when the table is used for comparative purity work, but should be taken into consideration in determining the sucrose content of juices and other liquors. Used understandingly, this table of Mr. Nikaido will prove most useful to all sugar chemists.

GEO. W. ROLFE.

THE ELEMENTS OF METALLOGRAPHY. By DR. RUDOLPH RUER. Privatdozent at the University of Göttingen. Authorized Translation by DR. C. H. MATHEWSON, Instructor in Chemistry and Metallography at the Sheffield Scientific School. New York: John Wiley & Sons. 1909. pp. xvi + 342. Price, \$3.

This volume represents a very desirable addition to the rather few text-books on metallography. The book is divided into two parts, the first of which is devoted to a discussion of the thermal equilibrium diagrams for one-, two- and three-component systems, most attention being paid to the binary alloys. Methods, other than thermal, for the investigation of equilibrium curves and for solidified mixtures are given in the supplement, and the discussion of the phase rule is also reserved for supplementary treatment. The explanations of the various types are given in great detail and the criteria for distinguishing the various constituents of an alloy, such as eutectic, compound, etc., are especially commendable.

The second part is devoted to the practice of metallography and deals with the thermal and structural investigation of alloys. A collection of references to about two hundred and seventy-five binary fusion diagrams of metallic alloys is given at the end of the book.

In spite of the general excellence of the work, there are some errors of translation which are liable to prove exceedingly confusing to the beginner, the portion dealing with the iron-carbon diagram being especially misleading. Thus by incorrectly translating "*zurückgegangen*" as "prominent", the translator would have the reader believe "that the tendency toward formation of incompletely stable crystalline varieties (cementite!) becomes very prominent in the case of alloys of appreciably higher carbon content than corresponds to B' (4.2 per cent. C)" and that this causes uncertainty as to the position of the curve representing primary separation of cementite from the melt. Such uncertainty is really caused not by the tendency of cementite to separate but from the prominent tendency of graphite to separate when the carbon content exceeds the above value.

Throughout this section "*Temperkohle*" is wrongly translated as "hardening carbon" instead of as "graphitic temper carbon."

The reviewer would scarcely agree with the translator that tempering effects a partial separation of cementite into ferrite and graphite, although annealing of high-carbon steels tends to produce this result.

In the preface the author states that the phase rule is reserved for the supplement on account of a disinclination on the part of the beginner to use it. In the reviewer's opinion there are other equally good reasons wherefore the student of metallography should early overcome such disinclination, first because the phase rule is undoubtedly the most easily applied and most general criterion as to the validity of any proposed system, and secondly, it is of almost universal occurrence in the literature dealing with heterogeneous equilibrium, especially as applied to alloys.

H. E. K. R.

THEORIEN DER CHEMIE. Nach Vorlesungen gehalten an der Universität von Kalifornien zu Berkeley. Von SVANTE ARRHENIUS. Mit Unterstützung des Verfassers aus dem englischen Manuskript übersetzt von ALEXIS FINKELSTEIN. Zweite, neubearbeitete und bedeut vermehrte Auflage. Leipzig: Akademische Verlagsgesellschaft m. b. H. 1909. pp. ix + 169.

The appearance of the first edition of this book has already been noticed in *THIS JOURNAL*.

The changes, and especially additions, that have been

made to the second edition can be best gathered from the author's own statement:

"Die rastlose experimentelle Arbeit, welche unsere Zeit auszeichnet, hat inzwischen sehr viel Material zu Tage gefördert, welches ich im Interesse des Lesers in dieser zweiten Auflage berücksichtigt habe. Besonders gilt dies für das Gebiet der Radioaktivität, welches für die theoretische Chemie von der grössten Bedeutung ist, da es einen Einblick in die Zusammensetzung der Atome gewährt. Auch die atomistische Auffassung der Materie ist durch die Forschung auf diesem und anderen Gebieten stark befestigt worden. Die Lehren von der Reaktionsgeschwindigkeit und von dem chemischen Gleichgewicht haben ebenfalls bedeutend an Umfang gewonnen und speziell auf dem wichtigen physiologisch-chemischen Gebiete grosse Landgewinne gemacht, die nicht ganz vernachlässigt werden konnten. Viele von den offenen Fragen sind durch eingehende Prüfungen, besonders von P. Walden, beleuchtet und teilweise erledigt worden. Alle diese Umstände führten dazu, dass die neue Auflage bedeutend umfassender geworden ist als die erste." H. C. J.

RECENT ADVANCES IN PHYSICAL AND INORGANIC CHEMISTRY. By A. W. STEWART, D.Sc., Lecturer on organic chemistry in the University of Belfast. Formerly 1851 Exhibition Research Scholar and Carnegie Research Fellow. With an Introduction by SIR WILLIAM RAMSAY, K. C. B., F. R. S. London, New York, Bombay and Calcutta: Longmans, Green & Co., 1909. pp. xiv + 267. Price, \$2.50.

The book is, as the author states, about equally divided between inorganic and physical chemistry, as the contents will show: Some hydroxylamine derivatives; Colloids; Reactions in liquid ammonia; The fixation of nitrogen; Double salts; The problem of the oceanic salt deposits; The cobalt-amines; Absorption spectra; The elements of the rare earths; Atomic weights; The inactive gases; The radioactive elements; Radioactive changes; Radioactive emanations.

In the two introductory pages by Ramsay several important matters are referred to. Ramsay likens Dr. Stewart "to a skilful cook who has trimmed his joint, rejecting all innutritious and redundant excrescences and has served it up to table in a palatable form. Such essays, I venture to think, will do more to encourage a taste for chemistry than many text-books."

Says Ramsay: "This book, it may be hoped, will have a still further use; it cannot be doubted that some who peruse it will have suggested to them various directions in which they may profitably attempt to increase knowledge. Nothing is



so sad as to see much time and labor spent, with patience and devotion, in the investigation of some matter which possesses no real importance. It may be retorted that every true statement is of importance, but this is not so. It is only statements which hold forth some prospect of contributing to an organic whole which can be held valuable. There may, perhaps, be a little more merit in ascertaining to the hundredth of a degree the boiling point of sulphur than of measuring the area of the wings of some particular butterfly; but the difference is barely appreciable. One is as likely to prove useless as the other. It would be well if enthusiasts anxious to carry on research would remember that it is much more stimulating to carry on an interesting than an uninteresting research. It is, I believe, not improbable that the reading of such a work as this may aid those imbued with the spirit of investigation to make a happy choice of a subject of research. Should this hope be realized, Dr. Stewart will have done a most useful work."

The book seems to be very well written and treats of the chosen chapters in an interesting way, but one notes the absence of a large number of subjects of fundamental importance for physical chemistry. Indeed, some of the subjects omitted seem to be of far more importance than some that are included in this work. However this may be, the book will doubtless serve a useful purpose.

H. C. J.

ÜBER DIE ERHALTUNG DER MASSE BEI CHEMISCHEN UMSETZUNGEN. Von H. LANDOLT. Abhandlungen der Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie. Herausgegeben im Auftrage der Gesellschaft von PROF. DR. R. ABEGB, in Breslau. Halle a/S: Verlag von Wilhelm Knapp. 1909. pp. viii + 47. Price, M. 1.80.

The results of this classical investigation of Landolt, on the question of whether there is a change in weight when chemical reaction takes place, are brought together in a very convenient form in this little monograph. This investigation, extending over seventeen years, is to be ranked among the most refined that have ever been carried out in chemistry, or in any other branch of science. The finest balances were used and the greatest care taken at every step in the work.

The conclusion drawn by Landolt from all of his work is as follows: "The final result of the entire work is that in the 15 chemical reactions studied, no change in weight could be shown to have taken place."

This work should be carefully studied by all who contemplate carrying on scientific research.

H. C. J.

BEITRÄGE ZUR KENNNTNIS DES ELEKTROCHEMISCHEN VERHALTENS DES EISENS. Von F. FOERSTER. Aus dem Laboratorium für Elektrochemie und physikalische Chemie an der Technischen Hochschule zu Dresden. Halle a/S: Verlag von Wilhelm Knapp. 1909. pp. 83. Price, M. 3.20.

This pamphlet is one of the *Abhandlungen der deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie*. The larger divisions are: The electromotive force of iron; The electrolytic separation of iron; and Electrolytic iron.

Some of the more interesting subdivisions are active iron, discussing also the condition of the "passive state;" active iron and the amount of hydrogen contained in it; iron rendering itself active; iron rendered active by the halogens; and the hydrogen content of electrolytic iron.

The section dealing with the "passive state" of iron is one of the most important in this monograph. The two theories of passivity that have attracted the greatest attention are: first, that the passive metal is covered with a layer of oxide, a view which is now scarcely tenable, and the reaction velocity theory, which says that ions of low valence dissolve slowly. The author thinks that the presence of hydrogen in iron and correlated elements has much to do with rendering these metals active.

The subjects dealt with are discussed in a clear, and, for the most part, attractive style.

H. C. J.



# AMERICAN CHEMICAL JOURNAL

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[Contribution from the Chemical Laboratory of the University of Wyoming.]

## THE REPLACEMENT OF HALOGEN BY THE NITRO GROUP.

[SECOND PAPER.]

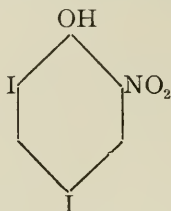
By L. CHAS. RAIFORD AND FRED. W. HEYL.

In a recent paper<sup>1</sup> we recorded the results of experiments in which an attempt was made to determine the relative activity toward nitrous acid of two of the symmetrical trihalogenated phenols, 2,4,6-tribromphenol and 2,4,6-trichlorophenol. The work was undertaken for the purpose of comparing the action of these compounds with the behavior of the corresponding halogenated *m*-cresols, the bromine compound of which had been found very reactive, giving a pair of isomeric mononitrodibrom-*m*-cresols, while the chlorine derivative was totally inactive under the same conditions. The reactivity of the halogenated phenols showed the same differences where the same halogens were involved, but the yields of the isomers obtained were much smaller than in the case of the cresols.

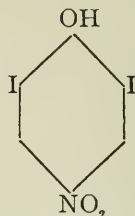
In view of these facts it became a matter of interest to examine the behavior of an iodine compound of this series. Accordingly, 2,4,6-triiodphenol was selected. Treatment of

<sup>1</sup> THIS JOURNAL, 43, 393 (1910).

this with nitrous acid in the manner specified below produced the two isomeric mononitrodiiodphenols:



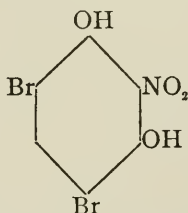
4,6-Diiod-2-nitrophenol,  
melting at 98°.



2,6-Diiod-4-nitrophenol,  
melting at 155°.

It is of interest here, also, to note that during this reaction more iodine was liberated than can be accounted for by the formation of a mononitrodiiod compound only, and that this indicates the possible production of some dinitromonoiodphenol. A second observation, which shows that triiodphenol is more reactive than the corresponding bromine compound, under the conditions of this nitration, is the fact that with the iodine compound a much smaller amount of unaltered substance was recovered from the reaction mixture.

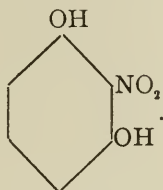
In a second set of experiments it was decided to study the behavior of a trihalogenated phenol containing two hydroxyl groups, and for this purpose 2,4,6-tribromresorcinol was chosen. When this compound was nitrated by the method used in these experiments, but a single nitro body was formed—a mononitrodibromresorcinol, melting at 148°. The only compound of this composition recorded by Beilstein was isolated by Weselsky and Benedikt,<sup>1</sup> who reported the melting point as 117°, and the structure as 4,6-dibrom-2-nitroresorcinol,



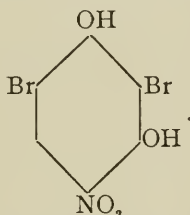
They obtained this compound by brominating a mononitro-

<sup>1</sup> *Monats. Chem.*, **1**, 886 (1881).

resorcinol which they found to be volatile with steam, and to which, on the basis of analogy to the volatile mononitrophenol, they assigned the formula



If the formulas assigned to these substances are correct, then our new nitro compound must be 2,6-dibrom-4-nitroresorcinol, and should be represented by the formula



The compound has been characterized by the preparation of several derivatives, and ultimately we shall determine the position of the nitro group. The results so far obtained are published at present because our work is now about to be interrupted for several months.

Further work has been outlined with the nitro compounds mentioned above, as well as with tribromacetanilide which, thus far, we have been unable to nitrate with nitrous acid; and with benzoyl-2,4,6-tribromanilide, which, according to Borrelli,<sup>1</sup> interacts with nitric acid to give two isomeric dinitro derivatives in which all the bromine is retained.

#### EXPERIMENTAL PART.

*Preparation of Starting Material.*—2,4,6-Triiodophenol was prepared by the method of Messinger and Vortmann,<sup>2</sup> which consists in a rearrangement of diiodphenoliod whereby the iodine atom bound to oxygen migrates to the ring. The

<sup>1</sup> Gazz. chim. ital., **17**, 527.

<sup>2</sup> Ber. d. chem. Ges., **22**, 2313.

change was brought about by boiling the diiod compound with a dilute solution of potassium hydroxide. From the resulting liquid, after filtration, quite pure triiodphenol was precipitated by the addition of hydrochloric acid. Crystallization from alcohol gave a pure product melting at  $158^{\circ}$ .<sup>1</sup>

Messinger and Vortmann<sup>1</sup> give  $156^{\circ}$  as the melting point.

Analysis for iodine gave the following results:

0.1706 gram substance gave 0.2559 gram AgI.

	Calculated for $C_6H_3OI_3$ .	Found.
I	80.72	81.04

*2,4,6-Triiodphenyl Acetate.*—The triiodphenol used in the nitration specified below was further identified by the preparation of an acetyl derivative. A portion of the substance weighing three grams was mixed with an equal weight of anhydrous sodium acetate, and the mixture heated gently with an excess of acetic anhydride, after which it was allowed to stand overnight. From the resulting solid, triiodphenyl acetate was extracted by boiling benzene, and from the solution obtained there separated colorless needles which after two further crystallizations from benzene melted sharply to a clear oil at  $154^{\circ}$ . A sample crystallized from chloroform melted at the same point. Analysis for iodine gave the following result:

0.2435 gram substance gave 0.3360 gram AgI.

	Calculated for $C_8H_5O_2I_3$ .	Found.
I	74.12	74.55

*Nitration of 2,4,6-Triiodphenol.*—In the experiments with triiodphenol it was early observed that this substance was not very soluble in glacial acetic acid at the temperature ( $12^{\circ}$ – $15^{\circ}$ ) at which these nitrations have been carried out; and subsequent tests showed that if acetic acid was added in sufficient quantity to prevent crystallization of triiodphenol during nitration, the volume of water into which the reaction mixture must be poured was so large that isolation of the nitro compounds involved much time and trouble.

<sup>1</sup> *Loc. cit.*

To avoid this difficulty a portion of the acetic acid was replaced by benzene, which readily dissolved triiodphenol and did not interfere with the reaction.

Twenty-one and nine-tenths grams of triiodphenol was dissolved in a mixture of 100 cc. glacial acetic acid and 200 cc. benzene. This liquid was cooled to  $12^{\circ}$ – $15^{\circ}$  and enough benzene added to dissolve any solid that had crystallized out. To this solution was next added, during half an hour, a ten per cent. excess of sodium nitrite, while the mixture was frequently shaken and the temperature carefully kept between  $12^{\circ}$  and  $15^{\circ}$ . The reaction mixture was allowed to stand overnight. At this point a portion of the liquid was removed, and the iodine that had been liberated during the reaction was shaken out with chloroform and titrated with standard solution of thiosulphate. The calculation showed that about five per cent. more iodine had been set free than was required by the production of a mononitrodiiod compound only, and this was thought to indicate the possible formation of a small amount of a dinitro derivative. The benzene was removed from the remainder of the mixture by evaporation under reduced pressure, and the residue, consisting chiefly of the glacial acetic acid solution of the nitro products, was poured into cold water. A black oil separated, which upon cooling congealed, and when removed from the greater part of the water and placed on a clay plate, finally solidified. The crude product weighed 15.7 grams, and its indefinite melting point indicated a mixture of substances.

#### *Separation of the Isomers.*

*The Ortho Compound.*—The method of separation used with the isomeric nitrodibromphenols, which involved the difference in solubility of the two substances in a mixture of chloroform and ligroin, was at first tried with the iodine derivatives, but it gave unsatisfactory results. The entire mass of crude product was next converted into potassium salts by boiling with one liter of aqueous solution containing 2.3 grams (one molecule) of potassium hydroxide. The two potassium salts thus formed were separated by a careful

systematic fractional crystallization. The salt of 4,6-diiod-2-nitrophenol separated first in the form of reddish brown needles that were practically pure. A portion was recrystallized from water, and after being dried to constant weight at  $110^{\circ}$  was analyzed for iodine.

0.2683 gram substance gave 0.2945 gram AgI.

	Calculated for $C_6H_3O_3NI_2K$ .	Found.
I	59.17	59.30

The first five fractions of this potassium salt, which together weighed about four grams, were separately decomposed by dilute hydrochloric acid, and each gave the mononitro-diiodophenol described by Körner,<sup>1</sup> which melts at  $98^{\circ}$ . From alcohol the compound crystallized in the form of bright yellow needles, which upon analysis for iodine gave the following results:

0.1318 gram substance gave 0.1582 gram AgI.

	Calculated for $C_6H_3O_3NI_2$ .	Found.
I	64.93	64.85

*Hydrochloride of 4,6-Diiod-2-aminophenol.*—The *o*-nitrodiiodophenol mentioned above was still further characterized by the preparation of its reduction product, which has not been described. This was secured as follows: The nitro compound was dissolved in the smallest possible quantity of boiling alcohol, and to the hot solution one-fourth more than the calculated amount of stannous chloride dissolved in concentrated hydrochloric acid (1 gram—1 cc.) was added. The mixture was then boiled until the color of the nitro body had been about discharged, after which an equal volume of concentrated hydrochloric acid was added and the whole allowed to stand. Upon cooling, the amino hydrochloride separated out. It was collected on a filter, dissolved in water, in which it is very soluble, and recrystallized by the addition of hydrochloric acid. In this way it was repeatedly crystallized until it was free from tin salt, when it separated in elongated prisms.

<sup>1</sup> Jahres. d. Chem. 1867, 617.



These were dried for several days over potassium hydroxide and then analyzed for halogen.

0.2279 gram substance gave 0.3518 gram AgHal.

	Calculated for $C_6H_5ONClI_2$ .	Found.
Halogen	72.80	72.83

*The Para Compound.*—When the filtrate from the salt of the ortho compound was evaporated it left a mass of greenish crystals that proved to be the potassium salt of the para compound. This was repeatedly fractionated, and the purest product thus obtained was decomposed by dilute hydrochloric acid, liberating 2,6-diiod-4-nitrophenol, which melted at about  $150^\circ$ . By several recrystallizations of this from alcohol it was obtained in nearly colorless prisms that melted sharply at  $155^\circ$ , and which gave the following results when analyzed for halogen:

0.1626 gram substance gave 0.1930 gram AgI.

	Calculated for $C_6H_3O_3NI_2$ .	Found.
I	64.93	64.18

The filtrate from the potassium salt of the para compound was acidified with dilute hydrochloric acid and gave a solid melting at  $156^\circ$ . A mixture of this substance and pure triiodphenol melted at the same temperature as either of them separately, which showed that the substance in question was unaltered triiodphenol. The amount recovered was much smaller than when tribromphenol was nitrated.

*Nitration of Tribromresorcinol.*—2,4,6-Tribromresorcinol<sup>1</sup> was prepared by mixing aqueous solutions of bromine and resorcinol in the theoretically required proportions, and was repeatedly crystallized from water until it melted constantly at  $112^\circ$ . Eleven and one-half grams of this product was dissolved in about twenty-five times its weight of glacial acetic acid, the solution cooled to  $12^\circ$ – $15^\circ$ , and then treated with sodium nitrite as already described. When about two-thirds of the nitrite had been added, a nitro compound (see below)

<sup>1</sup> Hlasiwetz and Barth: Ann. Chem. (Liebig), **130**, 357.

began to crystallize out. When all had been added and the mixture had been allowed to stand for half an hour in a cool place, the crystals, which after drying weighed three and one-half grams, were collected on a filter, and then crystallized twice from water, from which they separated in orange-colored needles melting at  $148^{\circ}$ . The acetic acid filtrate was now poured into five volumes of water, when a brown precipitate was formed. After standing some hours the mixture was filtered. The dried precipitate weighed 2.2 grams and contained 57.05 per cent. bromine, but since it did not have a sharp melting point and could not be obtained in crystal form, it was not further investigated. The filtrate was acidified with dilute sulphuric acid and extracted with chloroform. Evaporation of the latter left 3.6 grams of a brown residue which proved to be a mixture of tarry matter and a substance which could be crystallized from water, and was identical with the nitro compound mentioned above.

Analysis for bromine gave the following results:

0.2041 gram substance gave 0.2474 gram AgBr.

	Calculated for $C_6H_3O_4NBr_2$ .	Found.
Br	51.11	51.44

This nitro compound is acid in character, as shown by the salt formation specified below, and is nonvolatile with steam. It is readily soluble in alcohol, ether, chloroform, and benzene, but characteristic crystals could not be obtained from any of these liquids. From 30 per cent. alcohol maroon-colored prisms that melted at  $148^{\circ}$  were secured. Mixing these with the orange-colored needles caused no depression of the melting point. Analysis for bromine likewise indicated that the products were the same.

0.2434 gram substance gave 0.2905 gram AgBr.

	Calculated for $C_6H_3O_4NBr_2$ .	Found.
Br	51.11	50.80

*Ammonium Salt of Dibromnitroresorcinol.*—An attempt was made to further characterize this dibromnitroresorcinol by the

preparation of its salts. It forms sodium and potassium salts very readily, but both are so soluble that satisfactory crystals could not be obtained. A portion was dissolved in warm ammonia water and the solution allowed to stand in a warm place for several days. Upon evaporation of the excess of liquid, deep yellow prismatic crystals, that were free from water of hydration, were deposited. These were crystallized from water several times, dried to constant weight at  $110^{\circ}$ , and then analyzed for bromine. The results indicated a monoammonium salt.

0.1476 gram substance gave 0.1683 gram AgBr.

	Calculated for $C_6H_9O_4N_3Br_2$ .	Calculated for $C_6H_6O_4N_2Br_2$ .	Found.
Br	46.10	48.48	48.52

*Hydrochloride of Dibromaminoresorcinol*.—Five grams of the above nito compound were dissolved in hot alcohol and reduced with a hydrochloric acid solution of stannous chloride in the manner already described. The product that crystallized out was purified by treatment of its warm aqueous solution with concentrated hydrochloric acid, this process being repeated until the substance was practically colorless and no longer responded to a test for tin. It was dried for several days over potassium hydroxide and then analyzed for halogen and for nitrogen:

0.1792 gram substance gave 0.2912 gram AgHal.

0.1846 gram substance required 11.5 cc. 0.05 N HCl.

	Calculated for $C_6H_6O_2NClBr_2$ .	Found.
Halogen	61.18	61.18
N	4.38	4.36

*Dibromaminoresorcinol*.—The first attempt to prepare this free base was made by mixing with a water solution of the hydrochloride a slight excess of ammonium carbonate. A dark liquid, but no precipitate resulted. When a solution of the hydrochloride was mixed with a solution containing the theoretically required amount of sodium bicarbonate, the free amine was promptly precipitated in the form of a gray powder.

This was at once collected on a filter, washed several times with cold water, and then dried on a clay plate. From benzene the substance crystallized in prisms that were at first colorless, but which soon changed to gray. When heated above  $135^{\circ}$  it began to darken in color, and continued to blacken with rise in temperature; above  $175^{\circ}$  it decomposed without melting. Analysis for bromine gave the following results:

0.1419 gram substance gave 0.1897 gram AgBr.

	Calculated for $C_6H_5O_2NBr_2$ .	Found.
Br	56.53	56.88

*AcetylaminodibromresorcinyI Diacetate*.—This acetyl derivative was most conveniently prepared directly from the amino hydrochloride as follows: Equal weights of the hydrochloride and anhydrous sodium acetate were pulverized together, and upon this powder, in a small flask, was poured twice the theoretically required amount of acetic anhydride. Reaction began at once, as was indicated by a sharp rise in temperature, after which the mixture was boiled gently for about five minutes, and then set aside for twenty-four hours. At the end of this period the resulting solid was shaken with enough water to dissolve the sodium acetate, and the residue collected on a filter. Repeated crystallization from alcohol gave colorless hexagonal plates that melted at  $174^{\circ}$ – $175^{\circ}$ . The substance did not dissolve in a solution of sodium hydroxide and was regarded as a diacetate. Analysis for bromine confirmed this view:

0.1715 gram substance gave 0.1581 gram AgBr.

	Calculated for $C_{12}H_{11}O_6NBr_2$ .	Found.
Br	39.12	39.23

*Picrate of Dibromaminoresorcinol*.—The picrate of this amine was obtained by dissolving a portion of the hydrochloride in a saturated solution of picric acid and then allowing the mixture to stand. In a short time crystals in the form of dark green scales appeared. These were recrystallized from water in which they readily dissolve upon heating. When the sub-

stance was heated to 220° it began to decompose without melting. It was analyzed for bromine:

0.2156 gram substance gave 0.1552 gram AgBr.

	Calculated for $C_{12}H_9O_9N_4Br_2$ .	Found.
Br	31.23	30.63

Work has been outlined on the chlorine and iodine derivatives of resorcinol.

LARAMIE, WYOMING,  
May, 1910.

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## ON THE REARRANGEMENT OF THE TAUTOMERIC SALTS OF 1,4-DIPHENYL-5-THIONURAZOLE AND 1,4-DIPHENYL-5-THIOLURAZOLE.

[SEVENTEENTH COMMUNICATION ON URAZOLES.]

BY SIDNEY NIRDLINGER AND S. F. ACREE.

(We are indebted to the Carnegie Institution of Washington for aid in our research on tautomerism.)

Tautomeric compounds may be roughly classified under two heads;<sup>1</sup> first, those in which the equilibrium between the different forms is established very quickly in comparison with the velocity of the particular reaction being studied, and, second, those in which the equilibrium is established at a rate comparable with that of the reaction. The ideas of tautomeric equilibrium and especially of tautomeric salts, advanced by Acree<sup>2</sup> and collaborators, have made possible the quantitative study of the first case with results entirely in harmony with the theory. While the slow rearrangement of tautomeric acids and their final states of equilibrium have been measured by several investigators, no quantitative work has been done on the tautomeric salts of such acids, especially in the light of the theory of Acree. Such work should give a severe test for this idea and the results should be conclusive one way or the other. The most important work

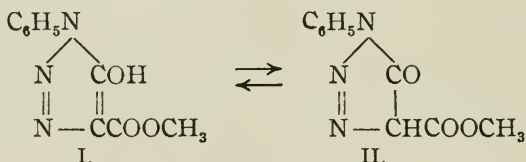
<sup>1</sup> See THIS JOURNAL, **43**, 361, 424.

<sup>2</sup> *Ibid.*, **37**, 71; **38**, 1; **39**, 124, 226. Ber. d. chem. Ges., **41**, 3199.

along this line has been done by Wislicenus,<sup>1</sup> Dimroth,<sup>2</sup> and Michael.<sup>3</sup>

Wislicenus, working on formylphenylacetic ester, was able to isolate a liquid enol and a solid keto form,<sup>4</sup> and to measure roughly the equilibrium between the two in a number of cases. He found that nondissociating solvents were favorable to that form which he called the enol or weaker acid form. The greater the concentration the more enol form he found in the solution. Starting with either form, under the same conditions of temperature and concentration, he found that the solutions are the same at the end of the reaction, thus showing that the rearrangement is perfectly reversible. His work on the salts was not very conclusive. The sodium salt made from either form liberated the so-called enol ester when precipitated with carbon dioxide, while with sulphuric acid the keto ester was liberated. Two different copper salts were also made but their exact constitution is doubtful.

The work of Dimroth<sup>5</sup> on methyl 1-phenyl-5-hydroxy-1,2,3-triazole-4-carboxylate was more conclusive owing to the fact that both tautomeric forms are stable solids, which in solution attain the following equilibrium:



The enol form (I) is a strong acid and liberates iodine quantitatively from potassium iodate and iodide in acid solution, while the keto form (II) is practically neutral. Dimroth found that the amount of the strongly acid enol form was greatest in the strongly dissociating solvents, this being in harmony with Wislicenus' results. In water, for example, the ratio of enol to keto is 1 : 14, in methyl alcohol 1 : 150,

<sup>1</sup> Ann. Chem. (Liebig), **291**, 147. Ahrens' Sammlung, II, 187.

<sup>2</sup> Ann. Chem. (Liebig), **335**, 1; **338**, 143.

<sup>3</sup> Michael and Hibbert: Ber. d. chem. Ges., **41**, 1080.

<sup>4</sup> This was afterwards shown by him, and also by Michael, to be a mixture.

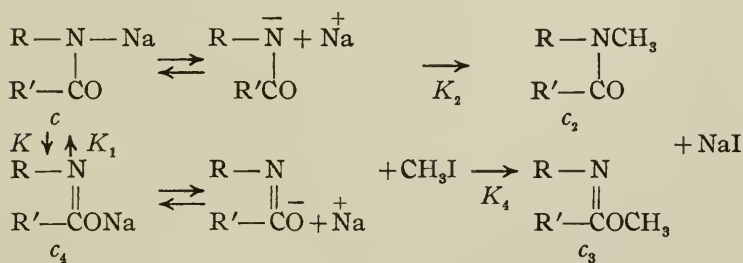
<sup>5</sup> Loc. cit.



in ethyl alcohol 1 : 300, while in chloroform, ether, etc., only the merest trace of enol form was found. An interesting fact observed was that the equilibrium was independent of temperature and concentration. In regard to the rate of rearrangement it was found that the change of the enol into the keto form was greatest in nonaqueous solvents, showing that the reaction was not due to the addition and splitting out of water. The molecular forms of the acids and not the anions were thought to be in direct equilibrium, as was also thought by Acree<sup>1</sup> to be true in the case of the salts of the urazoles, although the evidence for this is very meagre. No work could be done with the salts, as the keto ester is practically a nonelectrolyte and does not form stable salts.

Michael and Hibbert came to the conclusion that there is no direct connection between the equilibrium point, or velocity of change, of two tautomers and the physical constants of the solvents, such as the dielectric constant.

As we see, the work of Wislicenus, Dimroth, and Michael and Hibbert was concerned simply with the study of the rate of rearrangement and equilibrium of the acids themselves, and no attempt was made to study quantitatively and systematically the action of alkylating agents or other substances on either of the acids or their salts, or on an equilibrium mixture of the two. This is not a simple problem, as is shown by the following considerations:



In this scheme  $c$  is the original concentration of the keto form,  $c_4$  that of the enol form,  $c_1$  the amount of keto salt trans-

<sup>1</sup> THIS JOURNAL, **38**, 1. Wegscheider: *Z. physik. Chem.*, **35**, 518; **36**, 543. Goldschmidt: *Z. Elek. Chem.*, **11**, 5. Dimroth: *Ibid.*, **11**, 137.

formed into enol,  $c_2$  the concentration of the keto ester, and  $c_3$  that of the enol ester. Taking the simplest case first, suppose an equimolecular amount of methyl iodide is added to a solution containing a mixture of the two salts. We would have the following three reactions taking place:

(a) Sodium keto salt  $\rightleftharpoons$  sodium enol salt.

(b) Sodium keto salt and  $\text{CH}_3\text{I} \longrightarrow$  methyl keto ester and  $\text{NaI}$ .

(c) Sodium enol salt and  $\text{CH}_3\text{I} \longrightarrow$  methyl enol ester and  $\text{NaI}$ .

These would be represented by the differential equations:

$$\frac{dc_1}{dt} = K(C - C_1 - C_2) - K_1(C_4 + C_1 - C_3)$$

$$\frac{dc_2}{dt} = K_2(C - C_1 - C_2)(C + C_4 - C_2 - C_3)$$

$$\frac{dc_3}{dt} = K_4(C_4 + C_1 - C_3)(C + C_4 - C_2 - C_3)$$

In these equations  $K$  is the velocity constant for the change of keto salt into enol salt,  $K_1$  the constant for the reverse rearrangement,  $K_2$  that for the formation of keto ester, and  $K_4$  that for the formation of enol ester. The integration of these three equations would give a complete solution of the problem. This was not attempted, as the simultaneous alkylation and rearrangement was not studied. The differential equations for the case in which the salt rearrangement is not reversible, as well as for those in which the esters rearrange, have been worked out, but as they were not used in the work reported now, they will not be given. The above equations do not take into consideration the question whether the rearrangements or the alkylation reactions of the two tautomeric salts are ionic, or molecular, or both, side by side. If, however, the principle of isohydric solutions holds, the ratio of the concentration of the anions to that of the molecular salt should not change appreciably for either of the two forms in the solution, as we have sodium iodide formed in an amount equivalent to the sum of the keto

and enol salts disappearing by esterification. Then the different constants used above would equal the real reaction constants multiplied by  $\alpha$  or  $1-\alpha$ , according as the reactions are ionic or molecular or both, where  $\alpha$  is the percentage of ionization. Then, for example,  $K = (1 - \alpha) K'$ ,  $K_1 = \alpha K'_1$ , or  $K_2 = K'_2\alpha + K''_2(1 - \alpha)$ , when  $K'$ ,  $K'_1$ ,  $K'_2$  and  $K''_2$  are the true constants.

It is assumed that the rearrangement of the salt is a monomolecular reaction, as that seems to be made most probable by our work, described below, and that of Mr. E. P. Doetsch. The possibility, however, that the rearrangement is due to a union of the ions in the solution with the molecular form of the salt, or to other complex reactions, is not excluded, and this possibility is being investigated. In this case the rearrangement would not be monomolecular, although in some cases it might still apparently be so.<sup>1</sup>

The study of the slow attainment of equilibrium between the two forms of a weakly acid tautomeric substance should give most conclusive evidence as to the question of abnormal hydrolysis in the more concentrated solutions.<sup>2</sup> If we should add a solution containing an equilibrium mixture of the sodium salts, for example, to a solution of an equilibrium mixture of the free acids, we could easily calculate the total amount of each form in the solution, provided there was no abnormal hydrolysis. We could in some cases use conductivity methods. In other cases the whole mixture could be alkylated very quickly and the ratio of esters determined. If we have abnormal hydrolysis, the calculated should differ from the experimental values by an amount depending on the difference between the affinity constants of the two forms, the equilibrium constants, etc. The possibility of the influence of double salts, complex molecules, solvates, etc., must be carefully considered.

The compounds that first suggested themselves as being easily obtainable for our work were Dimroth's two forms<sup>3</sup>

<sup>1</sup> Acree and Nirdlinger: *THIS JOURNAL*, **43**, 358. Julius Meyer: *Z. physik. Chem.*, **66**, 81; **67**, 257.

<sup>2</sup> *THIS JOURNAL*, **43**, 365.

<sup>3</sup> *Ann. Chem. (Liebig)*, **335**, 1.

of methyl 1-phenyl-5-hydroxy-1,2,3-triazole-4-carboxylate. The enol form is a strong acid while the keto form is practically neutral. This would make it necessary, in esterifying a mixture of the two forms, to separate the keto form from the neutral ester formed, by converting it into the enol and extracting with an alkali. It was found that by rapid work the enol acid could be easily extracted from chloroform or ethereal solutions by means of aqueous solutions of potassium hydroxide, and the keto acid could be easily converted into the enol acid and extracted by treating the mixture with alcoholic solutions of potassium hydroxide. When the methyl enol ester, however, was treated by this method it was saponified to a considerable extent. For example, 0.1282 gram keto form and 0.1065 gram methyl enol ester were dissolved in chloroform, the chloroform evaporated, and the residue taken up in alcoholic potash. Then water was added and the solution extracted with chloroform and only 0.2 milligram of extracted substance was obtained. In another case from 0.1870 gram ester only 0.0059 gram of extract was obtained. In still another case in which the solutions were carefully cooled 0.1011 gram ester gave back 0.0672 gram unchanged ester. On this account the work had to be given up.

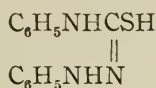
The compounds finally chosen for this work were the 1,4-diphenyl-5-thionurazole and 1,4-diphenyl-5-thiolurazole first described by Marckwald<sup>1</sup> and later by Busch<sup>2</sup> and his collaborators. A short summary of the evidence for the constitution of these compounds is necessary as our work has shown that the constitutions previously given are wrong. We should like to state at once that the work with these 5-thionurazoles is much more difficult than any that we have yet done. The properties of the compounds do not allow the development of very accurate quantitative methods, and added complications, due to the tautomeric changes going on, make the slow progress of the work sometimes very discouraging. Since these are the very phases of tautomerism that we wish

<sup>1</sup> Ber. d. chem. Ges., **25**, 3098; **29**, 2920.

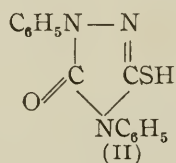
<sup>2</sup> Holzmann: Diss., Erlangen, 1902.

now to study, however, we shall continue the investigation of the problem.

W. Marckwald<sup>1</sup> found that by the action of phenylhydrazine on phenyl mustard oil in the cold, an  $\alpha$ -diphenylthiosemicarbazide was formed which melted at  $139^\circ$  and then rearranged into the  $\beta$ -semicarbazide melting at  $176^\circ$  described by E. Fischer.<sup>2</sup> Marckwald gave to this  $\alpha$ -semicarbazide formula (I) and the constitution of the thiourazole formed



(I)



(II)

by treating this with phosgene in the cold was thought to be represented by formula (II). This urazole melted at  $219^\circ$ – $221^\circ$  when crystallized from *hot* alcohol, and when treated with methyl iodide yielded an ester melting at  $185^\circ$  ( $196^\circ$  is the true melting point). This ester gave methyl sulphhydrate and the salt of 1,4-diphenylurazole when it was treated with potassium hydroxide, a reaction which showed that the methyl is attached to the sulphur atom. These points, especially the crystallization from *hot* alcohol, which causes a rearrangement, should be noted, as they are of considerable importance.

In the first papers<sup>3</sup> by Acree on the urazoles, it was stated that work was in progress on the 3-thio (or hydroxy)-5-hydroxy (or thio)urazoles, but this was stopped at that time in favor of Professor Busch. But the evidence which Acree<sup>4</sup> obtained proved beyond question that Marckwald's formulation for the constitution of the  $\alpha$ - and  $\beta$ -thiosemicarbazides and the above-mentioned thiourazoles was wrong. It was proved that the  $\alpha$ -1-phenylmethylthiosemicarbazide assumed by

<sup>1</sup> *Loc. cit.*

<sup>2</sup> *Ann. Chem. (Liebig)*, **190**, 122.

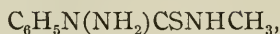
<sup>3</sup> *THIS JOURNAL*, **27**, 126. *Ber. d. chem. Ges.*, **35**, 556; **36**, 3139.

<sup>4</sup> The work which I have done since 1901 on these thiourazoles will be published soon. Professor Busch has in the meantime done far more, and better, work on these substances and cleared up beautifully some of the questions which are of great importance in this series of tautomeric substances.

S. F. ACREE.



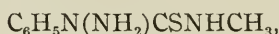
Marckwald to be the 1,4 compound, must be the 2,4 compound and have the formula



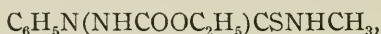
and that it rearranges, when heated in alcohol, especially in the presence of acids,<sup>1</sup> into the 1,4 compound having the formula



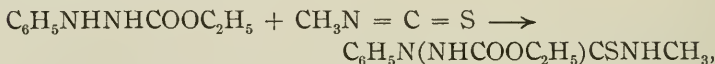
The proof, which was clear-cut, is the following: The  $\alpha$  compound,



when heated with ethyl chlorcarbonate in chloroform solutions, with or without sufficient sodium bicarbonate to neutralize the hydrochloric acid liberated, gave the ester



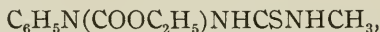
which, when treated with alkalies and then with an acid, yielded the 1-phenyl-4-methyl-3-hydroxy-5-thiourazole (A), which melted at 208°. This same ester was furthermore made by a reaction which could leave no doubt as to its constitution, namely, by the action of methyl mustard oil on phenyl carbazinic ester,



and when treated with alkalies as above it gave the same 1-phenyl-4-methyl-3-hydroxy-5-thiourazole, melting at 208°. But the  $\beta$ -phenylmethylthiosemicarbazide,



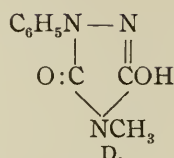
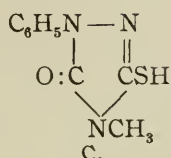
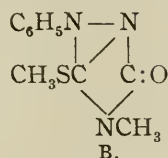
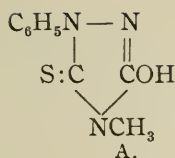
and ethyl chlorcarbonate in chloroform solution gave an isomeric ester,



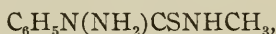
which, when treated with alkalies, etc., yielded an *isomeric* 1-phenyl-4-methyl-3-thiourazole (C), melting at 185°, which was also synthesized by an independent method.

<sup>1</sup> Ber. d. chem. Ges., **25**, 3098. We ask that the study of this and similar rearrangements be left to us.





These two isomeric urazoles, (A)<sup>1</sup> and (C), had therefore been synthesized by methods which could leave no doubt as to their constitution, or that the  $\alpha$ -semicarbazide is the 2,4-phenylmethyl-3-thiosemicarbazide,



and that the  $\beta$ -semicarbazide is the 1,4-phenyl-3-thiosemicarbazide,



instead of the stereoisomeric forms of the 1,4-phenylmethyl-3-thiosemicarbazide as assumed by Marckwald.

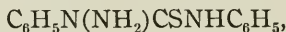
Furthermore, a comparison of the properties of our two isomeric 1-phenyl-4-methylthiourazoles left no doubt that Marckwald's 1,4-diphenylthiourazole melting at  $221^\circ$  was not a 3-thio compound, as assumed by him, but a 5-thio compound analogous to our 1-phenyl-4-methyl-5-thiourazole. The esters obtained by alkylating our 1-phenyl-4-methyl-5-thiourazole were certainly partially 5-thio alkyl compounds (B), because they gave a considerable quantity of 1-phenyl-4-methylurazole (D) and alkyl sulphhydrates when warmed with acid or alkaline solutions. They were therefore in every respect analogous to Marckwald's methyl ester melting at  $184^\circ$  (analogous to B), which he thought to be a 3-thiol methyl ester. That Marckwald's methyl thiol ester could not be a 3-thiol ester was further clear from the fact that of a large number of 3-thiol esters synthesized by Acree<sup>1</sup> by methods

<sup>1</sup> Ber. d. chem. Ges., **36**, 3139.

which left no doubt as to their constitution, *not one lost the alkyl sulphhydrate group to any appreciable extent when simply warmed with alkalies*, these compounds being particularly stable towards alkaline reagents.

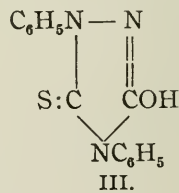
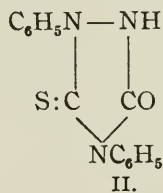
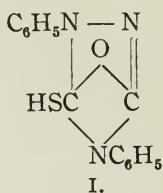
The evidence obtained by Acree shows conclusively then that Marckwald's so-called stereoisomeric thiosemicarbazides are the structurally isomeric 2,4- and 1,4-dialkyl-3-thiosemicarbazides, and that his so-called 1,4-diphenyl-3-thiourazole is in reality a 1,4-diphenyl-5-thiourazole.

But Busch<sup>1</sup> and Holzmann, in by far the best work then done on this problem, also came to the conclusion that the low-melting  $\alpha$ -semicarbazide has the constitution



which is, chiefly because of their work, generally accepted to-day.

These chemists and other coworkers obtained by the action of phosgene on the  $\alpha$ -diphenylthiosemicarbazide, a urazole acid which they supposed to be a 5-thiol<sup>2</sup> urazole (I). It melted, without further treatment, at  $141^\circ$ , and at this temperature, or on recrystallization from hot alcohol, rearranged into another form, which they assumed to have the constitution (II) or (III), or to be perhaps an equilibrium mixture of the two. This substance melted at  $219^\circ$ – $221^\circ$ , the fusion point of the compound obtained by Marckwald.

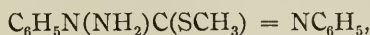


Busch and his colleagues believed that the low-melting urazole is a thiourazole (I), because it yielded, when treated with methylating agents, the methyl thiol ester (IV), which

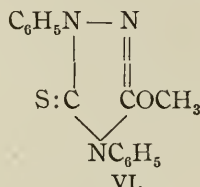
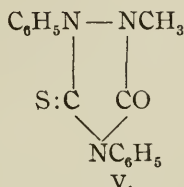
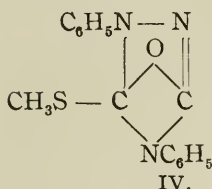
<sup>1</sup> Ber. d. chem. Ges., **34**, 326.

<sup>2</sup> See Ber. d. chem. Ges., **25**, 3098; **34**, 326, 340; **35**, 974. Holzmann: Diss., Erlangen, 1902. Grohmann: *Ibid.*, 1900. Reinhardt: *Ibid.*, 1906. Illgen: Dissertation, Berlin, 1894.

lost methyl mercaptan easily when treated with potassium hydroxide. Furthermore, they obtained the same methyl thiol ester, having undoubtedly this constitution, by treating the thiomethyl- $\alpha$ -semicarbazide,



with phosgene.



Reinhardt proved that the two forms of the acid give different sodium salts. He tried to methylate the two salts with methyl iodide, but heated the reaction mixture to  $100^\circ$  in a sealed tube and, as a result, in both cases he obtained an ester, melting at  $137^\circ$ , free from sulphur, of 1,4-diphenylurazole. He<sup>1</sup> found that on treating the sodium salt of the low-melting acid with dimethyl sulphate, an oily mixture was obtained. This is an important observation and should be kept in mind. The sodium salt of the high-melting acid, which he thought to have the constitution (II) or (III), gave with dimethyl sulphate the ester before mentioned melting at  $196^\circ$  and known to have the constitution (IV), corresponding to the urazole (I). He explained this discrepancy by stating that, on account of the vigorous action of the dimethyl sulphate, the acid of formula (II) is transformed into (I), which is more easily methylated. The silver salt of the acid melting at  $141^\circ$ , when treated with methyl iodide,<sup>2</sup> gave an oil which was not easily crystallized. The silver salt of the acid melting at  $221^\circ$ , supposed to have the constitution (II), under the same conditions gave (1) a small amount of an ester melting at  $133^\circ$ – $134^\circ$ , which did not split out mercaptan, and (2) much of the methyl thiol ester melting at  $196^\circ$ . This was also explained on the assumption that the silver is bound

<sup>1</sup> *Loc. cit.*, p. 72.

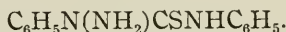
<sup>2</sup> *Loc. cit.*, p. 77.

partly to the sulphur, or that in the salt formation, some salt of the more reactive acid (I) was formed.

The work<sup>1</sup> described in the following pages was started provisionally on Busch's assumption that the low-melting acid has the composition (I) and the high-melting compound the composition (II). We were, however, soon forced to the conclusion that the low-melting acid is in reality 1,4-diphenyl-5-thionurazole, which can exist in two forms (II) and (III) in equilibrium, and that the high-melting form is a 1,4-diphenyl-5-thiolurazole, (I). This conclusion was reached for several reasons:

(1) In no case has the thiol methyl ester, (IV), corresponding to (I), been obtained from the pure low-melting acid, (II) or (III), in appreciable quantity. We have tested this point quantitatively and have never found more than 4 per cent. of this ester. The acid used by Marckwald,<sup>2</sup> which melted at 219°–221°, yielded a thiol methyl ester melting at 196°, and consequently was the form (I). Our own work amply confirms this conclusion. In every case the low-melting acid, (II) or (III), has, on esterification, given an oily product. This would be expected if it were the 1,4-diphenyl-5-thionurazole, which can exist in two forms, (II) and (III), and consequently would be likely to give a mixture of N-ester and O-ester, (V) and (VI).

In the presence of the phosgene the 2,4-diphenyl-3-thiosemicarbazide would function as a base and would react chiefly as



This should act with phosgene like all substituted ammonias and give first chiefly

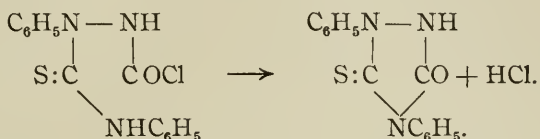


just as the phenylcarbazine esters do when treated with

<sup>1</sup> After Dr. Nirdlinger's work was finished in June, 1909, and reported at the Detroit meeting of the American Chemical Society in July, 1909 (Slagle and Acree: *THIS JOURNAL*, **42**, 123), Professor Busch wrote me in the autumn of 1909 and stated later in *Ber. d. chem. Ges.*, **42**, 4763, that he now believes, on account of his recent work, his former views to be incorrect. He now advocates the formulas deduced from the work in the present communication as being correct.—S. F. A.

<sup>2</sup> *Ber. d. chem. Ges.*, **25**, 3098.

phosgene.<sup>1</sup> The group  $\text{NHCOCl}$  could now, as an acid chloride, react with the weakly basic  $\text{NHC}_6\text{H}_5$  group, giving the 5-thionurazole:



The mechanism of the reaction by which the methyl ester of the 2,4-diphenyl-3-thiosemicarbazide gives the urazole methyl thiol ester (IV) when treated with phosgene<sup>2</sup> is not sufficiently clear to warrant any assumptions regarding the reaction. There is no doubt, however, that the urazole ester has the structure (IV).

(2) The high melting acid (I) gives the corresponding methyl thiol ester (IV), as would be expected if it had the structure (I) and not the thion structure (II) or (III), formerly assigned to it by Busch.<sup>3</sup> Busch's idea that the presence of the methyl thiol ester (IV) is due to a reverse rearrangement of the real thion acid, (II) or (III), on salt formation, is not in harmony with our data. For if the thionurazole rearranges into the thiolurazole in the presence of an alkylating agent and gives a corresponding thiol ester, it is hard to understand why the low-melting form, which Busch supposed to be the thiolurazole, always gives an oily mixture of ester, and never a thiol ester; if the thionurazole rearranges into the thiol acid and gives a thiol ester, the low-melting acid supposed by Busch to be a thiolurazole form should give this ester all the more readily.

(3) When the low-melting urazole, which when pure yields no thiol ester, is partially transformed, as indicated by a change in melting point, by heat or otherwise, into the high-melting acid, the resulting mixture yields on alkylation with alkalis and methyl iodide varying amounts of methyl thiol ester and less thion ester, depending upon the extent of the rearrangement.

<sup>1</sup> Heinrichs: Diss., Erlangen, 1900.

<sup>2</sup> Marckwald: *loc. cit.*; Busch and Holzmänn: Ber. d. chem. Ges., **34**, 340.

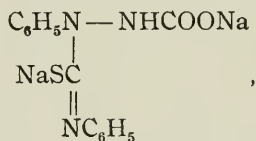
<sup>3</sup> Ber. d. chem. Ges., **34**, 326.

(4) The work of Doctors Brunel, Johnson, Shadinger, Rogers and Nirdlinger shows that the salts of the 3-thiourazoles react with alkyl halides many times as rapidly as the corresponding 3-hydroxy salts, practically pure thiol esters being formed. Using this as a diagnosis, we are forced again to the conclusion that the high-melting urazole ( $225^{\circ}$ ) is the 5-thiol form, (I), and the low-melting form ( $141^{\circ}$ ) is the 5-thion compound, (II) or (III). The sodium salt of the high-melting urazole ( $225^{\circ}$ ) reacts, in alcoholic solutions of methyl iodide, about 80 times as rapidly as does the sodium salt of the low-melting form ( $141^{\circ}$ ). This is shown quantitatively on pages 239-242.

The only point not worked out yet is the fact that the carbethoxy ester,



gives the high-melting form on treatment with an alkali,<sup>1</sup> while it might give the low-melting acid. Unfortunately we have not been able recently to secure this ester again in order to saponify it *in the cold* with alkalies and learn whether the urazole acid formed is really a pure thiolurazole or a mixture of the two urazoles with the melting point of the thiolurazole,  $225^{\circ}$  (see p. 236). When we consider, however, the grouping  $\text{R}(\text{CS})\text{NHC}_6\text{H}_5$  we see that in the presence of an alkali we could have part of the metal attached to the sulphur. The ester would be saponified and could give



which could, on addition of an acid, split out water and change partly into the corresponding thiol acid, just as the methyl ester of the  $\alpha$ -semicarbazide does when treated with phosphoric acid.

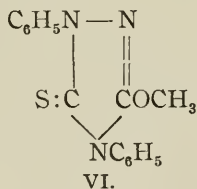
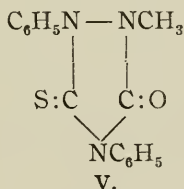
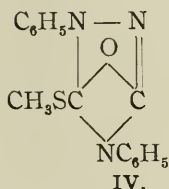
In order to show that certain samples of these acids give their own separate esters we give the following as an exam-

<sup>1</sup> Grohman: Diss., Erlangen, 1900, p. 15.



ple: The sodium salt from 0.202 gram of the low-melting acid gave 0.2022 gram methyl ester which contained only 0.0088 gram of methyl thiol ester, while the sodium salt from 0.202 gram of the high-melting urazole acid gave 0.1843 gram of methyl ester which contained 0.1628 gram methyl thiol ester. This shows conclusively that this sample of low-melting acid gave practically no thiol ester, and that the high-melting acid gave practically all thiol ester. This is what we should expect if the low-melting acid is 1,4-diphenyl-5-thionurazole, (II) or (III), and the high-melting acid, 1,4-diphenyl-5-thiolurazole (I).

Knowing now the real constitution of these urazoles, let us consider what we should expect of them in the light of the theory of tautomeric salts. Firstly, we could expect each salt to give its own individual esters by a direct reaction. Then the pure sodium 1,4-diphenyl-5-thionurazole could, and does, give on alkylation with methyl iodide a mixture of the N- and O-esters, (V) and (VI), just as 1-phenyl-4-methylurazole yields the two corresponding N- and O-esters:



In solution, however, the sodium 1,4-diphenyl-5-thionurazole could, and does, rearrange slowly into sodium 1,4-diphenyl-5-thiolurazole, which gives the methyl ester (IV). This ester, which contains the  $\text{SCH}_3$  group, should be, and is, very different from the two esters mentioned above, and can be separated quantitatively from them. Our problem then is to apply the proper equations to these reactions and determine whether we get constants as demanded by the theory. Whether we should use one equation or another depends on whether the rearrangement of the salts is reversible or not. Since it is not practicable to measure directly the ratio of the two salts in solution by conductivity or analogous methods, and

since the salts cannot be easily isolated from mixtures, the solution of the problem depends on the formation of stable derivatives from the two salts, the ratio of which can be measured. If we start with an individual salt, the problem would be to determine at any moment the ratio of thion to thiol ester formed. If, therefore,  $K$  and  $K_1$  (see page 221) are much smaller than the reaction constants ( $K_2$  and  $K_4$ ) of any alkylating agent, it would be only necessary to determine  $K$  and  $K_1$  independently by adding, for instance, a large excess of alkylating agent to a solution of the salt after any time period, and measuring the ratio of esters formed. In the same way,  $K_2$  and  $K_4$  could be determined independently by alkylating the pure salts under conditions such that there would be no appreciable rearrangement of these salts. In the case of these thiourazoles we have such conditions and this method can be used in all ordinary reactions of these compounds. Some alkylating agents, however, may be found, such that  $K$ ,  $K_1$ ,  $K_2$  and  $K_4$  will have nearly equal values, when the integrals of the general equations given on page 222 can be used.

If accurate analytical methods can be developed for studying these tautomeric 5-thion- and 5-thiolurazoles we shall take up at first the following problems:

(1) The relative velocities of reaction of the two tautomeric forms with other compounds, in different solvents, at different temperatures, etc.

(2) The relative velocities of the rearrangement of each salt into the other, in water and other solvents, at different temperatures, and hence the value of the equilibrium constants; many salts, having various anions and various cations, will be used.

(3) Especially will attention be given to the question whether all these reactions are ionic or molecular or both. It is very important to know whether only the anions of the salts, or the undissociated salts, or more complex ions or double salts, or *all*, rearrange into each other, and whether in the different individual cases the anions, or the undissociated salts (or the cations and anions together), or more complex

salts, or all together, may unite with the alkyl halides and form complex ions, or molecules, which can yield the end products.

All these questions are very complicated and can be solved only by a great amount of accurate work. Conclusions reached must be stated only tentatively and we are presenting our work and ideas only in this light. When our theory is no longer useful as a working hypothesis we shall throw it away.

#### EXPERIMENTAL.

*2,4-Diphenyl-3-thiosemicarbazide*.—This compound was made by the method of Busch and Holzmann<sup>1</sup>. To 10 grams of phenylhydrazine in 80 grams of alcohol, cooled in a mixture of salt and ice, 12.5 grams of phenyl mustard oil in 25 grams of cold alcohol were added. The semicarbazide separated out and after ten or fifteen minutes was filtered and washed with cold<sup>2</sup> alcohol. Twenty grams of pure compound melting completely at 139° were obtained.

*1,4-Diphenyl-5-thionurazole* was made by the method of Busch and Reinhardt.<sup>3</sup> One hundred and twenty grams of a 20 per cent. solution of phosgene in toluene, cooled in a mixture of salt and ice, were added to 10 grams of 2,4-diphenyl-3-thiosemicarbazide suspended in 20 cc. of half-frozen benzene. The mixture was shaken thoroughly and allowed to stand in a salt and ice mixture for a few hours, and then at the laboratory temperature. At the end of 48 hours the solid was filtered off, dried on a clay plate and shaken out in a funnel with a liter of very dilute cold caustic potash solution. Then the solid (*a*) remaining was filtered off and the alkaline solution was cooled in ice and acidified with cold dilute hydrochloric acid. The precipitated urazole (*b*) was filtered off immediately; when the filtrate was kept in ice more of the urazole (*c*) separated. The precipitate (*b*) obtained above was dried, shaken out with cold dilute alkali and filtered and the solution acidified. In this way 5 grams of urazole

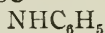
<sup>1</sup> Ber. d. chem. Ges., **34**, 324. Holzmann: Diss., Erlangen, 1902.

<sup>2</sup> This substance rearranges into the isomeric 1,4-diphenyl-3-thiosemicarbazide when it is crystallized from *hot* alcohol, but Mr. E. P. Doetsch has found that it can be nicely purified, without rearrangement, by crystallization from hot benzene.

<sup>3</sup> Reinhardt: Diss., p. 66.

were obtained; 2.5 grams from the second precipitation (*b*) and 2.5 grams from the filtrate (*c*). The substance melted completely when dipped into the melting-point bath heated to  $141^{\circ}$ , and then solidified and melted again at  $220^{\circ}$ – $222^{\circ}$ . The substance obtained from the filtrate (*c*) was perfectly white and dissolved in alkalis, forming a colorless solution, while the urazole which was reprecipitated (*b*) was slightly brown in color and gave a yellowish solution. The per cent. of thionurazole in each sample can be determined only by an analysis. Some samples contain 90 per cent. thionurazole and others were over 99 per cent. pure.

*1-Carbethoxy-2,4-diphenyl-3-thiosemicarbazide*,



.—An attempt was made to use this com-

pound for obtaining the 1,4-diphenyl-5-thiolurazole. The method of Busch and Grohmann<sup>1</sup> for making the semicarbazide was tried with no success. The following method gave good yields for a time: Twenty grams of 2,4-diphenyl-3-thiosemicarbazide were dissolved in 150 cc. of neutral chloroform in the presence of 25 grams of finely ground potassium carbonate and the mixture boiled under a return condenser. Then a slight excess of ethyl chlorcarbonate was added, and, after boiling one hour, half of the first amount of ethyl chlorcarbonate was added and the mixture boiled another hour. Then the chloroform solution was shaken out with water to remove the suspended potassium carbonate, dried, and the chloroform distilled off. An oil remained in the flask, which on standing deposited white crystals. Ether was added to the mixture, whereupon more crystals came out. They were filtered off and washed with ether; 7.5 grams of a substance melting at  $143^{\circ}$ – $144^{\circ}$  were obtained. The melting point of the compound of Busch and Grohmann was  $145^{\circ}$ . This substance was obtained several times with equally good yields when suddenly it became impossible to obtain any of it at all. At least 20 experiments were tried under varying conditions

<sup>1</sup> Grohmann: Diss., Erlangen, 1900, p. 20.

and with different solvents but in no case was any of the compound ever obtained again. No apparent reason for this was found. This trouble caused considerable delay in the work, as the compound would have furnished the 1,4-diphenyl-5-thiolurazole easily, in any desired quantity.

*1,4-Diphenyl-5-thiolurazole.*—This was first made by the saponification of the above ester. It was suspended in a small amount of alcohol and a slight excess of a solution of sodium ethylate added. The crystals soon went into solution, water was added and the solution was acidified; a voluminous precipitate of 1,4-diphenyl-5-thiolurazole was then formed. The substance, when crystallized from alcohol, melted at  $221^{\circ}$ – $223^{\circ}$ . After it was no longer possible to obtain the 1-carbethoxy-2,4-diphenyl-3-thiosemicarbazide, the thiolurazole was made by the rearrangement of the corresponding 1,4-diphenyl-5-thionurazole. For this purpose some of the 1,4-diphenyl-5-thionurazole was put into a test tube and dipped into a paraffin bath at  $150^{\circ}$  and kept there until it had fused and resolidified. Then it was dissolved in caustic potash and the solution filtered and precipitated with hydrochloric acid. The acid was filtered off and crystallized twice from alcohol. Then it was heated in a test tube to  $160^{\circ}$  for three hours in order to be certain that it was converted as completely as possible into the 1,4-diphenyl-5-thiolurazole. This was considered necessary, as a mixture of the two acids, containing about 50 per cent. of each, gives no sign of fusion when dipped into the melting point bath at  $143^{\circ}$ , and a mixture containing 80 per cent. of the 1,4-diphenyl-5-thionurazole barely shows signs of a fusion and resolidification wave traveling through the mixture at  $143^{\circ}$ . The substance was perfectly white and dissolved in alkalies, giving a colorless solution. It melted at  $221^{\circ}$ – $223^{\circ}$ .<sup>1</sup> *The constancy of the melting point gives no clue regarding the relative percentages of the thiol- and the thionurazoles, and these experiments should be borne in mind in all work on tautomeric compounds. The ratio can be determined only by an analysis, as discussed later, and when we speak of the thiol- and thionurazoles we do not*

<sup>1</sup> Reinhardt: Diss., 1906.



mean that they are necessarily free from each other, unless it is definitely so stated.

*Alkylation of 1,4-Diphenyl-5-thionurazole and 1,4-Diphenyl-5-thiolurazole with Diazomethane and -ethane.*—In the earlier part of the work it was intended to study the rearrangement of the two acids by adding a diazoalkyl, and analyzing the mixture of esters obtained. On studying the action of diazomethane and -ethane on the two urazole acids, however, it was found that the esters obtained are different from those made from the sodium salts and methyl iodide. None of them split out methyl sulphhydrate when heated with caustic potash, but they are decomposed, and give off hydrogen sulphide when the mixture is acidified.

Two grams of 1,4-diphenyl-5-thionurazole were suspended in ether and an ethereal solution of diazomethane was added until the yellow color of the diazomethane persisted. Then the ether was evaporated off. An oil remained which solidified on standing a week in a vacuum desiccator. The solid, after being washed twice with cold alcohol, melted at  $74^{\circ}.5-75^{\circ}.5$ . Analysis showed that it had the composition  $C_{15}H_{13}ON_3S$ . Yield, 1.2 grams. From 0.1210 gram of the ester heated 5 minutes at  $90^{\circ}$ , with a 3 per cent. solution of alcoholic potash, 0.015 gram of unchanged substance was obtained. Several other similar experiments were tried under different conditions of temperature, but with results of the same nature. One gram of 1,4-diphenyl-5-thionurazole under the same conditions gave, with diazoethane, an oil from which, on solidification and crystallization from alcohol, an ester melting at  $79^{\circ}-81^{\circ}$  was obtained. Yield, 0.5 gram. The analysis showed it to have the composition  $C_{16}H_{15}ON_3S$ .

Two grams of 1,4-diphenyl-5-thiolurazole, when treated with diazomethane, gave an ester which, when crystallized twice from alcohol, melted at  $129^{\circ}.5-130^{\circ}.5$  (uncor.). Analysis showed it to be isomeric with the ester obtained from 1,4-diphenyl-5-thionurazole and diazomethane: 0.1847 gram of this ester when heated one hour at  $100^{\circ}$  with 5 cc. of a 10 per cent. alcoholic solution of potassium hydroxide, gave back 0.0215 gram of unchanged ester. In another case, 0.0315



gram unchanged substance was obtained from 0.0864 gram ester on heating it 15 minutes at  $100^{\circ}$  with 5 cc. of 3 per cent. caustic potash. Results of a like character were obtained in experiments at  $50^{\circ}$ . 1,4-Diphenyl-5-thiolurazole and diazoethane gave an ester which, when crystallized from ligroin, melted at  $105^{\circ}.5-107^{\circ}.5$ . The fact that diazomethane does not give the 5-thiolurazole methyl ester melting at  $196^{\circ}$  is strong proof, with other such cases, that the diazoalkyls cannot be *absolutely* depended upon to give derivatives corresponding to the mother substance.

Owing to the fact that neither of the compounds obtained by treating the two acids with diazomethane reacted in a definite way with caustic potash it was impossible to separate the two, and consequently this phase of the work had to be abandoned. We shall later take up these reactions exhaustively. On account of the fact that diazomethane forms ring compounds with unsaturated substances, which double compounds may decompose further in some cases, it may be difficult to trace the relation between the constitution of the ester and that of the acid from which the ester is obtained.

*Preliminary Experiments on the Alkylation of Sodium 1,4-Diphenyl-5-thionurazole and Sodium 1,4-Diphenyl-5-thiolurazole.*—No attempt was made to isolate the sodium salts of the two acids, but in all cases the weighed amount of acid was titrated with the corresponding amount of sodium hydroxide. That this procedure can be used is shown by the following figures:

0.3983 gram of 1,4-diphenyl-5-thionurazole required 29.50 cc. 0.05 N NaOH. The calculated amount is 29.60 cc.

0.4050 gram of 1,4-diphenyl-5-thiolurazole required 30.20 cc. 0.05 N NaOH. The calculated amount is 30.08 cc.

Owing to the fact that Reinhardt<sup>1</sup> was unable to obtain the esters of the two acids from the sodium salts and methyl iodide the conditions governing the preliminary experiments were carefully watched. It was soon found, however, that at  $50^{\circ}$  or  $60^{\circ}$  or even at lower temperatures, large yields of

<sup>1</sup> *Loc. cit.*

the esters of the two acids can easily be obtained in a short time. It was simply necessary to add an alcoholic solution of methyl iodide to an aqueous solution of the sodium salt, and to heat this at  $50^{\circ}$  or  $60^{\circ}$  for an hour or two. Later when 20 molecules of methyl iodide (always in alcohol) were used, nearly quantitative yields of ester were obtained from each of the acids in 20 minutes.

The velocity of alkylation of the two salts with methyl iodide was first studied in order to obtain their relative reactivities. The procedure was as follows:<sup>1</sup>

1,4-Diphenyl-5-thionurazole (0.4039 gram) was weighed in a tube sealed off at one end and 3 cc. 0.5 N NaOH were run in from a burette. After the acid had dissolved, 2 cc. of 0.75 N solution of methyl iodide in ethyl alcohol were added, the tube sealed off, and put in the constant temperature bath and shaken. At the end of the time period  $t$ , it was taken out, cooled in ice water and opened, and the contents poured into an extraction funnel containing very dilute alkali. The ester<sup>2</sup> was extracted by shaking out the solution 6 times with chloroform. The chloroform was evaporated off below its boiling point in a weighed porcelain dish and the ester dried to constant weight,  $x$ , in a vacuum desiccator. The results of these quantitative experiments are given in Table I below.

That the extraction removes nearly all of the ester from the solution is shown by the following figures:

After 0.2955 gram methyl 1,4-diphenyl-5-thionurazole ester was extracted 6 times with dilute caustic potash, 0.2922 gram, or 98.87 per cent., was removed.

From 0.2949 gram methyl 1,4-diphenyl-5-thiolurazole, treated as above, 0.2920 gram ester, or 99 per cent., was recovered.

<sup>1</sup> Ber. d. chem. Ges., **41**, 3199.

<sup>2</sup> We have shown that this ester is a mixture of two thion esters—a N-ester [(V), page 233], and an O-ester [(VI), page 233]. We have not determined the ratios of these two esters, but this problem has been studied by Mr. E. P. Doetsch. The fact that this thion salt may be an equilibrium mixture of the  $=N-Na$  and  $-N=C(ONa)$  salt does not change the relations presented in this article.

Table I.—0.3 Wt. N Sodium Salt of 1,4-Diphenyl-5-thionurazole and 0.3 Vol. N Methyl Iodide in Ethyl Alcohol at 50°.

<i>t</i> (minutes).	<i>A</i> .	<i>x</i> .	<i>A</i> — <i>x</i> .	<i>AK</i> .
30	0.4249	0.1103	0.3146	0.0117
60	0.4249	0.1705	0.2544	0.0112
180	0.4249	0.2882	0.1367	0.0117
240	0.4249	0.3071	0.1178	0.0109

---

Average, 0.0114

The ester obtained was a viscous reddish oil, which, on standing, became semisolid.

The sodium 1,4-diphenyl-5-thiolurazole is so reactive with methyl iodide that no constants could be obtained at 50°. For example, 3 cc. 0.5 N sodium 1,4-diphenyl-5-thiolurazole and 2 cc. 0.75 vol. normal methyl iodide, at 50°, gave, in two hours, 0.3511 gram ester. In 5 minutes, at 25°, over 0.3 gram ester was obtained. In 15 minutes, at 60°, under the same conditions, 0.3584 gram ester was obtained, while in 4 hours only 0.3358 gram was found. This shows that practically all the ester is formed in a few minutes, and that it then slowly decomposes. This is also shown by the fact that on opening the tubes there was a strong odor of methyl mercaptan. The ester obtained was perfectly white and after one crystallization from alcohol and drying on the water bath melted sharply at 196°–197° to a clear, colorless liquid. It was identical with the ester obtained by treating 2,4-diphenyl-3-methylthiosemicarbazide with phosgene; a mixture of the two samples melted at 196°.

Since the thiol salt reacts so rapidly with methyl iodide at 25° or 50°, it was evident that the study of the reaction velocity must be done at 0°. The following table shows the data obtained in 50 per cent. alcohol by Mr. E. P. Doetsch.

If we assume a temperature coefficient of 2 for an increase of 10° *AK* would be 0.1344 at 50°. This means, when differences in concentration are considered, that the sodium thiol salt reacts about 80 times as rapidly with methyl iodide as does the sodium salt of 1,4-diphenyl-5-thionurazole.

Table II.—0.045 N Sodium Salt of 1,4-Diphenyl-5-thiolurazole and 0.045 N Methyl Iodide at 0°.

<i>t</i> (minutes).	A.	<i>x</i> .	A — <i>x</i> .	AK.
30	0.2394	0.0327	0.2067	0.00527
30	0.2394	0.0298	0.2096	0.00473
60	0.2394	0.0457	0.1937	0.00393
120	0.2394	0.0712	0.1682	0.00353
240	0.2394	0.1160	0.1234	0.00391
360	0.2394	0.1396	0.0998	0.00388
990	0.2394	0.2018	0.0376	[0.00540]
1265	0.2394	0.2097	0.0297	[0.00552]

Average AK = 0.0042

When the tubes were opened only a faint odor of mercaptan was observable, a proof that the thiol ester is hardly hydrolyzed at 0°.

*Hydrolysis and Separation of the Esters.*—Owing to the easy decomposition of the 1,4-diphenyl-5-methylthiolurazole by caustic potash into methyl mercaptan and potassium 1,4-diphenylurazole, it was at the beginning recognized that this would be the easiest way to separate this ester from a mixture containing it and the methyl esters of 1,4-diphenyl-5-thionurazole.

It was not so easy, however, to find an experimental method to hydrolyze this ester quantitatively, and at the same time not appreciably decompose the esters of the 1,4-diphenyl-5-thionurazole. In the preliminary experiments with 1,4-diphenyl-5-thiolurazole, a weighed amount of ester and enough alcohol to dissolve the ester was put in a porcelain dish on the water bath, and then various amounts of alkali were added. This method is easier than that involving the sealed tubes which we have used several years, although not so accurate. After a certain time the contents of the dish were washed into a funnel and the unhydrolyzed substance extracted with chloroform. Then the solution was acidified and the precipitated 1,4-diphenylurazole was extracted with chloroform and weighed as a check. The following results were obtained:

Weight of ester.	Amount of alkali.	Time heated (minutes).	Amount not hydrolyzed.	Per cent.	Per cent. of 1,4-diphenyl urazole recovered.
0.1995	10 cc. 0.25 N	20	0.0007	0.35	93.0
0.2047	10 cc. 0.50 N	20	....	....	92.2
0.1546	20 cc. 0.50 N	15	0.0004	0.25	96.0

This shows conclusively that the 1,4-diphenyl-5-methylthiolurazole can be hydrolyzed practically quantitatively. But when the oily esters of 1,4-diphenyl-5-thionurazole were treated by the above method they were not only badly decomposed, but the oil floated on top of the alkali and crept over the side of the dish. On this account the experiments in open dishes were abandoned. Then the methyl thiol ester was heated at 60° in sealed tubes with various amounts of alkali the tubes being shaken during the hydrolysis.

Weight of ester.	Amount of alkali.	Time of hydrolysis.	Amount not hydrolyzed (grams).	Per cent.
0.1460	10 cc. 0.25 N KOH	16 hrs.	0.0004	0.28
0.1017	10 cc. 0.10 N KOH	35 min.	0.0015	1.4

In the actual experiments, however, it is necessary to use chloroform in transferring the esters from the dishes in which they were weighed. The greater part of the chloroform is evaporated off, but one or two cc. always remain with the ester, and this is generally eliminated by repeated evaporation with small quantities of pure ether. Nirdlinger then introduced the "Künstgriff" of testing whether the methyl thiol ester could be hydrolyzed in the presence of chloroform in the tubes at 60°.

In the following experiment a weighed amount of 1,4-diphenyl-5-methylthiolurazole was put into tubes sealed off at one end and then 2 cc. chloroform and a certain amount of alkali were added. The tubes were sealed off at the other end and heated at 60°:

Weight of ester.	Amount of alkali.	Time of hydrolysis.	Amount not hydrolyzed (grams).	Per cent.
0.0835	10 cc. 0.1 N KOH	1 hour	0.0006	0.72

Then the methyl thion esters were treated in the same way.



These esters were obtained by alkylating sodium 1,4-diphenyl-5-thionurazole and extracting the ester with chloroform as explained before. After the ester had come to constant weight in the dish it was transferred to the small tubes drawn out to a capillary at one end, and the chloroform evaporated down to 1 or 2 cc. Then the tube was constricted at the other end, the alkali added and the tube sealed off. The tubes were heated at 60° with constant shaking:

	Weight of ester.	Amount of alkali.	Time of hydrolysis (hours).	Amount not hydrolyzed (grams).	Per cent. not hydrolyzed.
1	0.2477	10 cc. 0.1 N KOH	1	0.2385	96.2
2	0.2950	10 cc. 0.1 N KOH	1	0.2883	97.7
3	0.1724	10 cc. 0.1 N KOH	1	0.1684	97.6
4	0.1684	10 cc. 0.1 N KOH	1	0.1674	99.4

In experiments 1, 2 and 3 the ester was taken in the condition in which it was obtained from the action of methyl iodide and sodium 1,4-diphenyl-5-thionurazole. We should expect some loss here due to the formation of the methyl thiol ester from that part of the salt which rearranged into the other form during the alkylation, and from some of the thiol salt present originally. Experiment 4 is of especial importance, as in this case the ester remaining after hydrolysis in experiment 3 was used. This is the real test of our method and we see that in the presence of the chloroform the methyl esters of 1,4-diphenyl-5-thionurazole are not appreciably attacked by dilute caustic potash at 60°.

Then experiments were tried with mixtures of the methyl esters. The procedure was that used above, the methyl thiol ester being weighed into the tubes before the other ester had been washed in by means of chloroform:

Thiol ester.	Thion ester.	Alkali.	Weight of unhydrolyzed ester.	Time.
0.0623	0.2278	8 cc. 0.25 N KOH	0.2291	2
0.0510	0.2258	8 cc. 0.25 N KOH	0.2255	2

By this procedure, then, the esters are separated quantitatively, the methyl thiol ester being hydrolyzed and giving methyl sulphydrate and 1,4-diphenylurazole, while the oily methyl esters of 1,4-diphenyl-5-thionurazole remain in the



chloroform and are not greatly affected by the alkali. The 1,4-diphenylurazole can be recovered to the extent of about 95 per cent. by acidifying the aqueous solution in the funnel, and extracting with chloroform.

It was at once realized that if the esters were to be used as a means of analyzing the mixture of salts at any moment a method must be devised for alkylating the salts quantitatively in a short time and giving a ratio of esters corresponding to the ratios of the two salts. Since other researches in the urazole group have shown that the ratio of esters may change with the change in solvent we decided to try first a mixture of water and alcohol. Mr. E. P. Doetsch has since learned that the presence of the alcohol has a serious disturbing effect on the apparent ratios of the salts, and that the hydrolysis of the thiol ester during the alkylation must be suppressed by making the solution *neutral* by adding a mixture of mono- and disodium phosphates or other similar compounds. The results of the present investigation must therefore be considered as preliminary.

After various experiments it was found that 20 molecular equivalents of methyl iodide and either salt, in about 7 cc. of 60 per cent. alcohol, will give practically quantitative yields of ester, at 60°, in from 15 to 20 minutes. From 0.404 gram 1,4-diphenyl-5-thionurazole, 0.417 gram methyl ester was obtained. The theoretical amount is 0.425 gram. Furthermore, 0.404 gram of 1,4-diphenyl-5-thiolurazole gave 0.409 gram ester under the same conditions. Then the two salts (0.2 gram) were alkylated and the esters analyzed in order to determine the purity of the acids used:

*1,4-Diphenyl-5-thionurazole.*

	Weight of ester.	Weight of ester after hydrolysis.	Loss.	Per cent purity of acid.
1	0.2022	0.1934	0.0088	95.65
2	0.1976	0.1914	0.0062	96.86

*1,4-Diphenyl-5-thiolurazole.*

1	0.1690	0.0198	0.1492	88.29
2	0.1843	0.0215	0.1628	88.34
3	0.1818	0.0195	0.1623	89.3
4	0.1843	0.0187	0.1656	89.86

It is seen in this last table that the alkylations were not complete. As a final check on the method, known weights of the two acids were mixed, the theoretical amount of sodium hydroxide added and the salts alkylated. Then the esters were analyzed. In calculating the actual amount of each acid in the mixture the 1,4-diphenyl-5-thionurazole was taken as being 96.25 per cent. pure, and the 1,4-diphenyl-5-thiolurazole as being 89 per cent. pure:

Weight of 1,4-diphenyl-5-thionurazole (1) (gram).	Weight of 1,4-diphenyl-5-thiolurazole (2) (gram).	Calculated per cent. of (1) in total acid.	Found.
0.1020	0.100	53.9	55.6
0.0455	0.1565	30.5	31.7
0.1465	0.0555	72.6	71.5
0.1000	0.1020	52.9	53.5
0.1500	0.0520	74.2	73.6

The check experiments described in this section show that the method, taken as a whole, is accurate to well within 5 per cent. A more systematic study of the time and the concentration of alkali necessary for complete hydrolysis of the methyl thiol ester, and the conditions for complete alkylation of the salts, would without doubt reduce the maximum error to 2 or 3 per cent. The results of the rearrangement experiments described below appear, on the surface, to be very satisfactory. Such, however, is not the case and this fact must serve as a warning against the hasty acceptance of mere mathematical concordance of the results. In this physical-organic research there are so many uncertainties until each problem is studied deeply that the conclusions can be only tentative.

*Rearrangement Experiments.*—While the method of analysis of the salt mixtures was being worked out, preliminary experiments were made on the rearrangement of sodium 1,4-diphenyl-5-thionurazole. The first experiments were carried out at 100°. Three cc. of a 0.5 weight N solution of sodium 1,4-diphenyl-5-thionurazole were sealed in a small tube holding about 6 cc. and the tube was fastened in the neck of a flask half full of rapidly boiling water. After certain intervals the tubes were opened and 2 cc. of 0.75 vol. N methyl iodide

in ethyl alcohol<sup>1</sup> were run in and the tubes were sealed up again. This made the whole solution approximately 0.3 N. After heating two hours at 60° the contents of the tubes were poured into extraction funnels and the esters were extracted with chloroform and weighed. In one experiment lasting twenty-two hours, practically pure methyl ester of 1,4-diphenyl-5-thiolurazole was obtained on alkylation, so no further work was done at 100°. Then tubes were heated in the same way at 60° and alkylated. After heating one tube eleven hours and then alkylating, 0.201 gram of ester was obtained which contained 80 per cent. of the esters of 1,4-diphenyl-5-thionurazole. Although only about half of the salt had been alkylated, this indicated very well that the reaction could be studied at 60°.

Meanwhile the method for the analysis of the mixture of salts had been worked out, so the procedure finally adopted was as follows: 0.202 gram of 1,4-diphenyl-5-thionurazole was weighed into a tube holding about 8 or 9 cc. and the tube was drawn out to a long capillary at the open end. Then 1.5 cc. of 0.5 N sodium hydroxide and 1.5 cc. of water were run in and the tubes sealed off. This made the solution 0.25 weight N with respect to the salt. The tubes were put into a bath<sup>2</sup> kept at 60° for certain time periods and then taken out. The very tip of the capillary was broken off and 4 cc. of 3.75 vol. N methyl iodide were run in, the capillary was sealed up again and the tube then put back into the bath. At the end of twenty minutes it was taken out, opened, and the contents were poured into a separating funnel containing water to which a few drops of alkali had been added. The ester was extracted with 6 portions (5 cc. each) of chloroform, the chloroform was evaporated off in a weighed porcelain dish, and the ester was then dried to constant weight at 55° in an air bath. The ester was transferred by means of chloroform to small tubes, drawn off to a capillary at the lower end, and

<sup>1</sup> As stated above, the alcohol should not be used. Mr. E. P. Doetsch has shown that when the alcohol is present there is a more rapid change of the ratio of the salts during the alkylation than when water alone is used. While our results are fairly concordant, they are only tentative.

<sup>2</sup> For a description of the bath used see Brunel and Acree: *THIS JOURNAL*, **43**, 533.

the solvent was evaporated down to about 2 cc. by dipping the capillary part of the tube into a water bath at 80°. *To prevent bumping a capillary stirring rod is inserted well down into the capillary end of the tube.* Then 5 or 6 cc. of half-normal potassium hydroxide were added and the tubes sealed off. They were shaken for two hours in the 60° bath, and opened, and the unhydrolyzed ester extracted in the usual way. The following table shows the results obtained in a large number of experiments:

Table III.

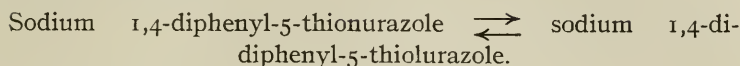
Time (hours).	Weight of total ester.	Weight of unhydrolyzed ester.	Per cent. thion ester (C—C <sub>2</sub> ).
0	0.1976	0.1914	96.8
	0.2022	0.1934	95.7
6	0.1987	0.1775	89.3
	0.2010	0.1800	89.5
12	0.2058	0.1652	80.3
	0.2037	0.1625	79.8
18	0.2110	0.1565	74.2
24	0.2007	0.1410	70.4
	0.1977	0.1374	69.7
36	0.1705	0.1083	63.5
	0.1945	0.1230	63.2
42	0.2013	0.1192	59.2
96	0.1726	0.0556	32.3
	0.1618	0.0516	31.9
168	0.1584	0.0384	24.2
216	0.1732	0.0343	19.8
	0.1686	0.0319	18.9
336	0.2019	0.0204	10.1

Experiments were carried out in the same way with sodium 1,4-diphenyl-5-thiolurazole.

Table IV.

Time (hours).	Weight of total ester.	Weight of unhydrolyzed ester.	Per cent. thion ester (C—C <sub>2</sub> ).
0	0.1690	0.0198	11.7
0	0.1843	0.0215	11.7
0	0.1818	0.0195	10.7
0	0.1843	0.0187	10.1
48	0.1868	0.0214	11.5
120	0.1760	0.0280	15.9
	0.1805	0.0295	16.3

These figures show that the reaction is slightly reversible and that we have:



If the reaction is monomolecular<sup>1</sup> then

$$(1) \quad \frac{dc_2}{dt} = K_1(C - C_2) - K_2(C_1 + C_2),$$

where  $C$  is the original concentration of the sodium 1,4-diphenyl-5-thionurazole,  $C_1$  that of the sodium 1,4-diphenyl-5-thiolurazole present at first, and  $C_2$  that of the rearranged salt.

At equilibrium,

$$\frac{K_1}{K_2} = \frac{C_1 + C_2}{C - C_2}$$

Substituting  $\frac{K_1}{K_2} = K$  in equation (1) and integrating we get

$$\frac{1}{t} \log \frac{KC - C_1}{KC - C_1 - (K + 1)C_2} = K_1 + K_2.$$

Since in a unimolecular reaction the unit of concentration is immaterial we can assume that  $C$  is 96.25 and  $C_1$  is 3.75. The experiments given above do not give the definite equilibrium ratio but the most probable one is the value for sodium 1,4-diphenyl-5-thionurazole heated for 336 hours, where  $C_2$  is equal to 96.25-10.1, or 86.15. Then,

$$K = \frac{K_1}{K_2} = \frac{3.75 + 86.15}{96.25 - 86.15} = 8.9$$

Table V.

$T.$	$C.$	$C_1.$	$C_2.$	$K_1 + K_2.$	$K_1.$	$K_2.$
6	96.25	3.75	6.9	0.0061	0.0055	0.00061
12	96.25	3.75	16.3	(0.0076)	(0.0068)	(0.00076)
18	96.25	3.75	22.1	0.0071	0.0064	0.00071
24	96.25	3.75	26.3	0.0066	0.0059	0.00066
36	96.25	3.75	33.0	0.0058	0.0052	0.00058
42	96.25	3.75	37.1	0.0060	0.0054	0.00060
96	96.25	3.75	64.2	0.0062	0.0056	0.00062
168	96.25	3.75	72.3	(0.0047)	(0.0042)	(0.00047)
216	96.25	3.75	76.9	(0.0045)	(0.0041)	(0.00045)

<sup>1</sup> In the equations no account is taken of the question whether the molecules or the ions of the salts undergo transformation. In either case it would merely be necessary to substitute for  $c$  and  $c_1$  the values  $\alpha c$  or  $(1-\alpha)c$ , and  $\alpha'c_1$  or  $(1-\alpha')c_1$  and hence introduce new constants. According to the isohydric principle  $\alpha$  and  $\alpha'$  should be practically constant during the reaction. It is also not greatly material whether  $c$  or  $c_1$  represents a mixture of two salts in nearly instantaneous equilibrium.

This series, while only preliminary, shows apparently that the reaction is monomolecular and especially that the salts rearrange into each other. It is especially to be regretted that in many of the experiments in the above tables the weight of ester is much below the theoretical. As stated above, however, Mr. E. P. Doetsch has obtained better results where no alcohol is present.

#### *Conclusions.*

1. It has been shown that the compound supposed by others to be 1,4-diphenyl-5-thiolurazole is in reality 1,4-diphenyl-5-thionurazole, and that the one supposed by them to be 1,4-diphenyl-5-thionurazole is 1,4-diphenyl-5-thiolurazole.

2. This work shows that we can convert these two acids into salts which have two different tautomeric forms, one corresponding to the structure of 1,4-diphenyl-5-thionurazole and the other corresponding to the structure of 1,4-diphenyl-5-thiolurazole. These two salts not only give back their corresponding acids on the addition of hydrochloric acid, but they also give their own characteristic derivatives. The silver salts of the two acids are also different. The two sodium salts have each been alkylated with equivalent amounts of methyl iodide. The sodium 1,4-diphenyl-5-thionurazole and methyl iodide in 0.3 N solution (40 per cent. alcohol) at 50° give a very good constant,  $AK = 0.0114$ , only about 75 per cent. of the salt being alkylated in 4 hours at 50°. The sodium 1,4-diphenyl-5-thiolurazole is alkylated 75 per cent. in 5 minutes at 25°, while this salt and methyl iodide in 0.045 N solution (50 per cent. alcohol) at 0° give the constant  $AK = 0.0042$ . If we assume a temperature coefficient of 2 for each 10° and take into consideration differences in concentration, the experiments show that methyl iodide reacts about 80 times as rapidly with the sodium salt of 1,4-diphenyl-5-thiolurazole as it does with the other sodium salt, and this fact gives further evidence that we have assigned the correct structure to the higher-melting form.

3. The sodium salts of these two acids have been esterified



quantitatively and a method, accurate to within 5 per cent., has been devised for analyzing a mixture to the two salts. A mixture of the esters can be analyzed accurately with an error of 2 or 3 per cent.

4. It is shown further that the sodium salts are mutually convertible into each other through two apparently reversible unimolecular reactions, and that the velocity of rearrangement of the sodium 1,4-diphenyl-5-thionurazole is approximately 9 times as large as that of sodium 1,4-diphenyl-5-thiolurazole. The thiol salt is less reactive in this reversible change but much more reactive in the alkylation experiments. A study of the relationship of the energy changes involved in the two reactions is of the greatest importance.

5. Work with these compounds should throw great light on tautomerism. We can actually isolate the tautomeric acids and their corresponding salts, and can study accurately many of the tautomeric phenomena exhibited by these substances. Other types of tautomeric compounds, such as acetacetic ester, cyanides, cyanates, nitrophenols, phenolphthaleins, oximes, amidines, and many others, whose properties do not so readily admit of such quantitative study, exhibit many of the tautomeric phenomena belonging to the urazoles. It is therefore possible that further work on these urazoles will help us to understand more about the large number of classes of substances known under the name of tautomeric compounds.

JOHNS HOPKINS UNIVERSITY,  
BALTIMORE, June 1, 1909.

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## THE DIFFUSION OF CRUDE PETROLEUM THROUGH FULLER'S EARTH.

BY J. ELLIOTT GILPIN AND OSCAR E. BRANSKY.<sup>1</sup>

### INTRODUCTION.<sup>2</sup>

It is a well-established fact that the petroleum obtained from the sandstones of the Upper Devonian and Mississippian

<sup>1</sup> Dissertation submitted to the Johns Hopkins University by Oscar E. Bransky for the degree of Doctor of Philosophy.

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periods, generally known as the Pennsylvania oil, differs markedly from the natural oil found in the Trenton limestone, usually designated as the Ohio oil, or Trenton limestone oil. Both of these oils, in turn, are distinctly different from the petroleum occurring in the loose sands and soft shales of California. The unconsolidated tertiary clays, sands, and gravels in the southern United States, particularly in Texas, yield another variety of petroleum, characterized by properties more or less different from any of the preceding oils.

Not only do these differences exist between oils found in separate regions, but extreme variations in color and specific gravity, as well as in chemical composition, often occur between those of neighboring localities. On the other hand, close resemblances abundantly occur between petroleum of sections widely removed from each other. Some of the South American and many of the European oils, for instance, have been found to possess properties very similar to those of the oils of the southern United States; while the oil from the Corniferous limestone of Canada closely resembles the Ohio petroleum.

These variations in the oils of the United States and other countries have been carefully studied by many investigators. Such noted workers as Warren, Storer, Mabery, Pelouze, Cahours, Schorlemmer, Beilstein, Markownikoff, Engler, and Kurbatoff have devoted their lives to this subject. The question that naturally arises in connection with these variations is: Are these differences fundamental? Is the Pennsylvania petroleum as distinctly different from the Ohio oil as one chemical compound is from another? In answer to these questions, the following extract from a paper read by Mabery<sup>1</sup> in 1903 before the American Philosophical Society is of considerable importance: "Now, after years of arduous labor, I have reached the conclusion that petroleum from whatever source is one and the same substance, capable of a simple definition—a mixture of variable proportions of a few series of hydrocarbons, the product of any particular field differing from that of any other only in the proportion of the series and the members of the series." The evidence supporting

<sup>1</sup> P. Am. Phil. Soc., 1903.

this declaration has been and is accumulating constantly, and, at the present time, this view is generally accepted.

If petroleum, then, is one and the same substance, how can the extreme variations between the American oils be explained? Were the causes operating in the formation of the Pennsylvania oil, almost barren of sulphur and nitrogenous bodies, different from those acting in the production of the sulphur-bearing oils of Ohio, or the heavy sulphur and nitrogenous oils of California?

To account for the formation of crude petroleum, two views, as is well known, the organic and inorganic, have been advanced. The Pennsylvania oil, according to these theories, may have been formed either from organic or inorganic substances, or from both. It is as yet impossible, however, to state conclusively from which of these sources the oil was derived. It is apparent, therefore, that the differences between the Pennsylvania and the Ohio, Texas, and California oils cannot be explained upon the assumption that the former was formed from organic remains, while the latter were produced from inorganic matter, or *vice versa*. If, however, crude petroleum is organic in origin, it may have been formed either from vegetable or from animal remains. The following discussion is based upon the assumption that the above-mentioned oils were derived from an organic source.

It has been suggested that the differences between these oils may be accounted for by assigning a vegetable origin to the Pennsylvania oil, and an animal origin to the others. Mabery<sup>1</sup> states that "It would seem that the small proportion of these bodies<sup>2</sup> in the Pennsylvania oil, as compared with the larger proportions in the limestone oils and California oils should be strong evidence in favor of a different origin, that the Pennsylvania oil came from organic vegetable remains, which should permit of the small amounts of sulphur and nitrogen compounds from this class of oils." Newberry, Peckham, Orton, and other geologists also favor the view that the Pennsylvania oil is of vegetable origin, and is derived

<sup>1</sup> P. Am. Phil. Soc., 1903.

<sup>2</sup> Reference is made to the sulphur, nitrogen, and oxygen compounds in petroleum.

from the organic matter of the bituminous shales of the Devonian period.

The facts which have led to the association of this oil with a vegetable source are, first, that the oil is of a different character from the limestone oils of Ohio, and those of Texas and California; second, that the Pennsylvania petroleum is found in strata that bear but few fossils; third, the belief that the Chemung and immediately overlying formations are barren of animal organic remains; fourth, the existence of large quantities of microscopic fossils, whose origin many believe to be vegetable, in the black shales of the Lower and Middle Devonian periods, to which formations many investigators are inclined to refer the origin of the Pennsylvania oil.

It is generally recognized that the Pennsylvania oil differs markedly from the Ohio, Texas, and California oils. Investigation has shown that the former contains a much larger proportion of the paraffin hydrocarbons, and a much smaller percentage of benzene and unsaturated hydrocarbons and sulphur and nitrogenous bodies, than the latter oils. It is further generally admitted that the Pennsylvania oil was not formed *in situ*. These two facts have aided strongly in assigning a vegetable origin to this oil. To what strata, then, should the source of the oil be referred? The great coal formations of Pennsylvania, lying above the Chemung, seem, at a first glance, to offer a solution of this problem. It is a notable fact, however, that these formations have not, up to the present time, been connected, either chemically or geologically, with the Pennsylvania oil. The possibility exists, however, that it was formed from vegetable remains in the Carboniferous formations above, and that then, by downward diffusion, it reached its present position in the Chemung. This view rests upon the physical fact that a liquid diffuses by the force of capillarity in all directions, downward as well as upward. Little attention has been given to this possibility, but it seems to deserve a very careful study. Owing, however, to the universal association of water under hydrostatic pressure with natural oil and gas, the migration of the latter is generally upward. This fact is attested by the accumulation of oil

in anticlinal folds when water is present, and by the existence of the remarkable gushing oil wells. That the Pennsylvania oil, if not formed *in situ*, ascended to its present location seems, therefore, more probable.

In what strata below the Chemung, then, was the oil originally produced? It has been previously mentioned that a number of investigators refer the source of the oil to the black shales of the Lower and Middle Devonian periods. The organic matter of these shales is composed largely of microscopic sporangites, which suggest the existence, according to Orton, of masses of floating vegetation, or Sargasso seas. According to this view, the origin of the Pennsylvania oil is vegetable in character, and its primitive abode was in the shales of the Devonian age lying below the Chemung sandstone, to which it ascended under the influence of natural agencies. Another origin, animal in character, may be assigned to this oil. This view is that the oil was formed in the fossil-bearing strata of the Chemung age, and that it diffused to the sandstone reservoirs in which it is now found, and that during such a diffusion its original character was changed. Prof. C. K. Swartz, of the Johns Hopkins University, who has made a critical study of the Chemung strata in Maryland, informs us that fossil remains exist in considerable abundance in the strata of this age in Maryland and adjoining areas. In Pennsylvania, the corresponding strata have been found to bear many fossils. It is possible that the oil formed in these strata, and then diffused to the strata in which it now exists and which are barren of fossil remains.

The evidence accumulated in this investigation seems to show that it is not necessary to assign a vegetable origin to the Pennsylvania oil to explain the differences between it and the oils of Ohio and California. It is clear from the results of this and other investigations that, when such oils as those of Ohio and California and Texas, which seem to be of animal origin, are allowed to diffuse through such porous media as fuller's earth, they yield oils very similar to those of Pennsylvania. By assuming, therefore, that the Pennsylvania oil migrated from some primitive source, in which it may



have been formed from animal remains, through shales, limestones, and sandstones, its peculiar character can be understood.

Whatever the original home of the oil, it seems probable that it migrated to its present location from some place below. It is with the changes occurring in crude petroleum as a result of such a migration through porous strata that the present investigation is primarily concerned.

In 1897, Dr. David T. Day,<sup>1</sup> from his own observations, and those of Dr. John N. MacGonigle, proposed the view that the Pennsylvania oil, at some past time, possessed properties very similar to those of the Ohio oil, but that in its migration to its present abode from regions below, its character was changed to its present condition.

Guided by this view, he conducted, in the laboratories of the United States Geological Survey, an investigation into the changes occurring in crude petroleum when allowed to diffuse through porous media, such as fuller's earth. He demonstrated clearly that an oil resembling the light Pennsylvania oil could be readily produced in the laboratory from the heavier crude Ohio oil. Glass tubes were packed firmly with the dry earth, through which the crude oil diffused by its own force of capillarity. From the earth of the upper sections of the tubes, very light, in some cases colorless, oils were liberated by treatment with water; from the earth of the lower sections of the tubes, much darker and heavier oils were obtained.

It will be observed that the fractionation is effected entirely by capillarity; oils with different surface tensions rise with different velocities through the capillary openings, such as the fine interstices and minute pores of the fuller's earth. A separation of the various constituents making up the complex of any one oil is thus produced. The view once held that this phenomenon is chemical was clearly disproved by Engler and Albrecht<sup>2</sup> in 1901, and later by other investigators.

<sup>1</sup> P. Am. Phil. Soc., 1897.

<sup>2</sup> Z. angew. Chem., 1901, 889.



Any medium, therefore, sufficiently fine-grained and porous to afford capillary spaces causes a separation of the constituents of any mixture, provided they possess different surface tensions. The compact sandstones, shales, and limestones that recur in many cycles throughout the earth's crust present an excellent medium for the separation of the constituents of such a complex mixture as petroleum. The force of capillarity, assisted by the hydrostatic pressure of the water occurring in the interior of the earth, acting over vast periods of time, is, it seems safe to state, sufficiently powerful to transport the oil from the lower regions to those above. That the conditions, therefore, to cause such a migration, with the consequent fractionation of the original oil, are abundantly present, appears extremely probable.

Let us examine, now, the conduct of the constituents of petroleum subjected to such a fractionation. The members composing the natural oil may be grouped under the following general heads: paraffin, aromatic, unsaturated hydrocarbons, sulphur, nitrogen, and oxygen compounds. The behavior of the paraffin and unsaturated hydrocarbons will be considered first.

Dr. David T. Day early observed that the unsaturated hydrocarbons are less diffusible than the paraffin hydrocarbons. Later, Gilpin and Cram clearly demonstrated that when petroleum is allowed to diffuse through tubes packed with fuller's earth, the unsaturated hydrocarbons collect in the earth of lower sections of the tubes, while the paraffins tend to accumulate in the lightest fraction at the top of the tube. In the present investigation, these results have been fully confirmed. On pages 296 to 299 are given the bromine absorption values, and the percentages by volume absorbed by concentrated sulphuric acid of the various oils obtained from definite sections of a tube. These figures indicate conclusively that the amount of unsaturated hydrocarbons in the oils from the lower sections of the tube is much greater than the amount of these hydrocarbons in the lightest fractions at the top of the tube. Furthermore, the bromine absorption values for the oils of similar fractions of the first, second, and third frac-

tionation, given on page 298, show that in the progress of the fractionation more and more of the unsaturated hydrocarbons are removed. Herr,<sup>1</sup> in Russia, has likewise observed that these hydrocarbons are less diffusible than the paraffins.

An interesting confirmation in Nature of these experiments has been recently presented by Clifford Richardson and K. G. MacKenzie.<sup>2</sup> They found that a colorless natural naphtha from the Province of Santa Clara, Cuba, contained practically no unsaturated hydrocarbons, but was almost entirely a mixture of naphthenes and paraffins. Concentrated sulphuric acid absorbed but 0.76 per cent. by volume, while fuming sulphuric acid absorbed only 1.8 per cent. With the naphtha were obtained water and an emulsion of water, oil and clay. These investigators are of the opinion that the naphtha was "undoubtedly formed by the upward filtration of heavy petroleum through the clay stratum, similar to the fuller's earth filtrations of Gilpin and Cram, and the light naphtha in the upper part of the stratum was afterwards partly liberated by saline waters, the oil remaining in the clay forming with water the emulsion."<sup>2</sup>

A comparison of the proportions of unsaturated hydrocarbons in Ohio and Pennsylvania oils shows that the latter contains a much smaller percentage of these hydrocarbons. By assuming that the Pennsylvania oil diffused upward through such porous media as shales and limestones to its present location in the sandstones, it is possible to account for the smaller amounts of the olefins in it on the basis of the experimental work described above. In its passage through the capillary interstices of the clays, limestone and sandstones, a fractionation, resulting in the removal of the unsaturated hydrocarbons, probably occurred. It is reasonable to conclude, therefore, that the variation in the content of unsaturated hydrocarbons between the Ohio, Texas, and California oils, on the one hand, and the Pennsylvania oil on the other, can be probably accounted for by assuming that the latter was subjected to capillary diffusion at some time in its career.

<sup>1</sup> Petroleum, August, 1909.

<sup>2</sup> Am. J. Sci., May, 1910.

That the light-colored naphthas occurring in various parts of the world were originally darker and heavier oils, and that their primitive character was changed by diffusion through media possessing the power of fractionation, seems very probable.

The behavior of the aromatic hydrocarbons, in particular benzene, in passing through fuller's earth, constitutes one of the subjects of this investigation. The results of this study, given in detail on pages 269 to 276, indicate clearly that benzene, like the olefins, tends to collect in the lower sections of a tube of fuller's earth through which the benzene, in solution, is allowed to diffuse. That the aromatic hydrocarbons in the natural oil behave in a similar manner has not yet been decided. The proportion of these hydrocarbons in the Illinois oil investigated was too small to enable us to determine accurately their amounts in the various fractions obtained by the capillary diffusion of the crude oil. The ordinary methods, such as nitration with a mixture of nitric and sulphuric acids, and sulphonation, employed for the quantitative determination of the aromatic hydrocarbons, could not be used in this work, owing to the fact that these reagents readily affect the unsaturated hydrocarbons as well. A study of the conduct of the aromatic hydrocarbons in the natural oil containing large amounts of them will be undertaken in the near future. It is probable, however, that the benzene and homologous compounds in crude petroleum behave like the unsaturated hydrocarbons.

The presence of larger amounts of aromatic hydrocarbons in the Ohio than in the Pennsylvania petroleum, and still larger amounts in the California and Texas oils, seems to afford further evidence in favor of the view that the Pennsylvania oil has undergone much greater diffusion, and consequently greater fractionation, than any of the other oils.

The conduct of the sulphur compounds in petroleum in the process of diffusion is similar to that of the unsaturated hydrocarbons. On pages 298 to 299, the percentages of sulphur present in the oils from different parts of the tube and different

stages of fractionation are tabulated. One series of figures will be given to show the behavior of the sulphur compounds:

Lot 6. Fraction	Per cent. of sulphur.	
	First fractionation.	Third fractionation.
A	0.04	0.003
" B	0.05	...
" D	0.09	...
" E	0.16	...

It is clear from these figures that the sulphur compounds, like the unsaturated hydrocarbons, tend to collect in the lower sections of a layer of fuller's earth through which petroleum is allowed to diffuse.

In 1902, Clifford Richardson and E. C. Wallace,<sup>1</sup> in an investigation on the occurrence of free sulphur in Beaumont petroleum, passed this oil upward through the kaolin filter described by Dr. D. T. Day at the Petroleum Congress in Paris, in 1900, and obtained a distinct fractionation. The percentages of sulphur in the crude oil, and the oils obtained by this fractionation were determined. The results are given in the following table:

	Sp. gr. 25°/25°.	Per cent. sulphur.
Crude oil	0.9140	1.75
1st fraction	0.8775	0.70
2nd fraction	0.8986	0.91
3rd fraction	0.9038	1.04

It seems reasonable to assume from these results that the variations in the sulphur content between the Pennsylvania and Ohio oils may be satisfactorily explained by the view that the former oil, as previously stated, diffused from other regions to its present location, and in its migration a large part of its original content of sulphur was removed. Further work upon this point will be undertaken in this laboratory.

No careful study of the behavior of the nitrogen and oxygen compounds in petroleum diffusing through a porous medium has as yet been undertaken. A careful investigation of this matter will be pursued in this laboratory later on.

<sup>1</sup> J. Soc. Chem. Ind., March, 1902.

It is probable that such an investigation will show that the nitrogen compounds conduct themselves like the sulphur and unsaturated compounds.

*The Object of this Investigation.*

The present investigation was undertaken for the immediate purpose of studying the changes occurring in the crude Illinois oil when allowed to diffuse through fuller's earth. The more distant, but more fundamental, object was to gain further insight into the causes of the variations between the various oils of this country.

EXPERIMENTAL.

*Preliminary Experiments.*

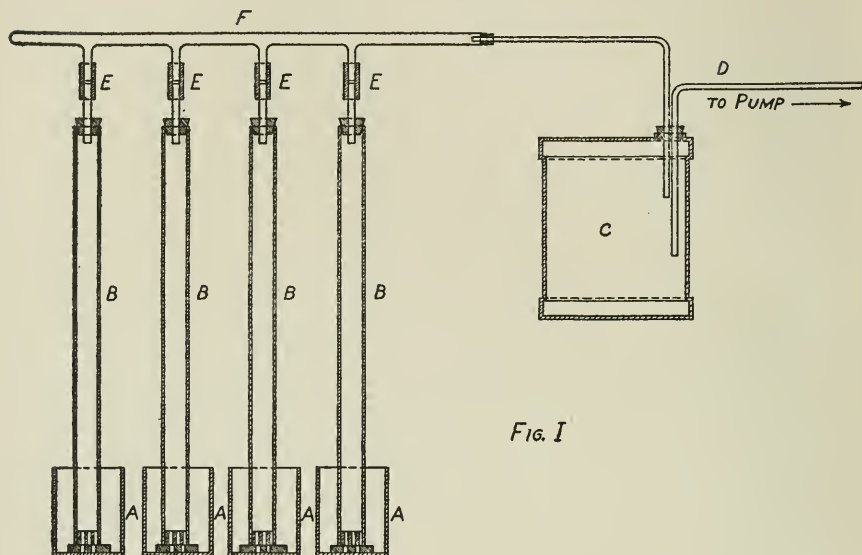
*The Relative Amounts of Oil Lost in Heated and Unheated Fuller's Earth.*—Before the actual investigation of the Illinois oil was undertaken, experiments were made to determine the relative amounts of oil lost in heated and unheated fuller's earth.<sup>1</sup> In the work of Gilpin and Cram, the earth was always heated until geysers ceased to form, and then allowed to cool for several hours. The purpose of heating the earth was to obtain larger yields of oil, but towards the close of their investigation it became apparent that the amount of oil lost in unheated fuller's earth was not as large as they had supposed it to be. Since much time and labor is consumed in the process of heating and then cooling the earth, it seemed advisable to settle this point at the outset.

*Apparatus.*—The apparatus employed for this investigation was essentially the same as that used by Gilpin and Cram. *A, A, A, A* (Fig. I) are tin reservoirs made to hold somewhat more than a liter. The tin tubes *B, B, B, B*, 5.5 feet in length, and 1.25 inches in diameter, rest upon narrow tin supports placed upon the bottom of the reservoirs, and are connected with the branched glass tube *F* by suction tubing fitted with pinchcocks at *E, E, E, E*. The tube *F* is connected with the large tank *C*, which serves to maintain fairly constant pressures; *C* is in turn joined by the glass tube *D*

<sup>1</sup> The fuller's earth employed in these investigations was generously supplied by the Atlantic Refining Company of Philadelphia.



to a manometer, and the latter connected with the Chapman pump. Any number of these tubes may be set up in series under the same diminished pressure.



*FIG. I*

After the tubes are closed at their lower ends with grooved corks covered with muslin to prevent the earth from sifting out, they are packed to the desired firmness with the fuller's earth. Each tube is then placed in its own reservoir, containing the oil to be fractionated. When they are connected to the branched tube *F*, the pressure in the system of tubes is reduced by the suction pump. The oil rises at first rapidly, then its diffusion gradually diminishes in power. When the reservoirs are almost exhausted, the tubes are disconnected and clamped, with the bottom ends up, above shorter tubes of the same diameter, into which the oil-laden earth is allowed to slide. These shorter tubes are made of two curved pieces, joined at the bottom by a cap, and held together at the top by a ring. The cylinders are opened by slipping off the ring and cap and removing one of the curved pieces, and the earth divided into the desired sections. When water is added in



portions to the earth and the two mixed thoroughly, the oil is displaced and is drawn off in separate portions.

Six tubes packed with heated fuller's earth were set up alternately with six tubes filled with the unheated earth. Each tube was placed in its own reservoir containing 950 cc. of crude oil. The oil was allowed to diffuse upward through the tubes under diminished pressure. Sixteen hours elapsed before the oil in the reservoirs was exhausted. Since the tubes did not rest directly upon the bottom of the reservoirs, a small amount of oil remained, the volume of which was subtracted from the volume originally supplied. The earth from each tube was shaken into a bucket, and the oil recovered by displacement with water, as described above. The results of these experiments are given in the following table:

*Table I.—Heated Fuller's Earth.*

Tubes.	Weight of fuller's earth. Grams.	Oil absorbed by earth. cc.	Oil recovered. cc.	Oil lost. cc.	Per cent. oil lost. cc.
1	1005	850	450	390	46
3	1000	792	460	332	41
5	1035	850	500	350	41
7	1070	865	450	415	48
9	1035	813	430	383	47
11	1045	885	530	355	41
Total,	.....	5055	2830	2225	44

*Unheated Fuller's Earth.*

2	1075	917	585	332	36
4	1095	853	562	291	34
6	1065	840	500	340	42
8	1045	814	435	379	46
10	1035	873	510	363	41
12	1055	850	485	365	41
Total,	.....	5147	3077	2070	40

The petroleum employed in the above experiments was a dark, green oil from Venango County, Pennsylvania, possessing a specific gravity of 0.810.

Since the Illinois oil, which was used in the fractionation proper, described later, differs materially from the Pennsyl-



periments, the percentage of oil lost in the unheated is smaller than that lost in the heated earth, Gilpin and Cram, employing heated earth, recovered, in one test, 5,951 cc. from 9,070 cc., and, in another, 5,415 cc. from 8,915 cc., the amount of oil lost in the earth in the first test corresponding to 34 per cent., in the second to 39 per cent. It is clear, therefore, that there is no sufficient, if any, compensation for the time and labor spent in heating the earth. In the investigations that followed, herefore, the unheated fuller's earth was always used.

*The Diffusion of Benzene in Solution through Fuller's Earth.*—

In order to deal more intelligently with the fractionation of the crude Illinois petroleum, it seemed advisable to study the behavior of the individual aromatic hydrocarbons, especially benzene, both alone and mixed with paraffin hydrocarbons, when allowed to diffuse upward through fuller's earth. Gilpin and Cram established the fact that the paraffin hydrocarbons tend to collect in the lightest fractions at the top of the tube. Their method consisted in distilling by heat six samples of oils of different specific gravities, each 300 cc. in volume, and collecting ten fractions between definite intervals. Five of these samples consisted of oil partly fractionated by fuller's earth, and the other of the crude oil. The specific gravity and viscosity of each fraction were determined; then to 30 cc., or to all there was where the amount was less than 30 cc., an equal volume of concentrated sulphuric acid (specific gravity 1.84) was added, and the two shaken in a machine for half an hour or longer. The volume of the oil unaffected by the acid was measured, and, by subtraction, the volume of oil absorbed was calculated. This latter volume represents only approximately the percentage of unsaturated hydrocarbons present in the oil, because sulphuric acid of this strength readily dissolves benzene when the two are thoroughly shaken.

In this investigation various solutions of benzene and a refined paraffin oil, boiling between 160° and 240°, and only slightly attacked by sulphuric acid, were made up and allowed to rise in tubes packed with unheated fuller's earth. The

pressure in the system was reduced very little, because the liquid, under a greatly diminished pressure, rose too rapidly. About 24 hours elapsed before the oil in the reservoirs was exhausted.

The earth in each tube was shaken out and divided into six sections. Beginning at the uppermost point to which the oil had ascended, grade *A* consisted of the first 8 cm.; grade *B* of the next 8 cm., grade *C* of 18 cm.; grade *D* of 30 cm.; grade *E* of 35 cm.; and, finally, grade *F* of the remainder of the earth, depending on the height to which the oil had ascended. This division is the same as that used by Gilpin and Cram. The oil in the earth was displaced by water and drawn off.

The specific gravity of each fraction was determined by means of the Mohr-Westphal balance at exactly 20°. The fourth decimal is not to be considered as strictly accurate, but gives a closer approximation to the truth than if it were entirely discarded.

The viscosity was determined by means of the viscosometer described by Ostwald and Luther and modified by Jones and Veazey.<sup>1</sup> The time taken for measured volumes of the oils to drain from the small bulb, whose capacity was 4.5 cc., was compared with the time required for a similar amount of water to run through. These values were substituted in the equation

$$\gamma = \gamma_0 \frac{TS}{T_0 S_0},$$

where  $\gamma_0$  = coefficient of viscosity of water. For this, 0.01002, the value obtained by Thorpe and Rodger,<sup>2</sup> was used.

$t$  = time of flow of liquid under examination.

$S$  = specific gravity, measured at 20°, of liquid under examination.

$T_0$  = time of flow of water.

$S_0$  = specific gravity of water. Since the balance was calibrated for water, at 20°, the value for  $S$  is unity.

$\gamma$  = coefficient of viscosity of oil under examination.

<sup>1</sup> Z. physik. Chem., **61**, 351.

<sup>2</sup> Phil. Trans., A, **185**, 397 (1894).

The amount of benzene present in each fraction was determined by shaking the oil with an excess of ordinary concentrated sulphuric acid (specific gravity 1.84) for periods of time varying from 30 to 60 minutes, until there was no further diminution in the volume of the oil.

The following experiments demonstrate the power of this acid to dissolve benzene, forming benzenesulphonic acid:

(1) Twenty-five cc. of benzene were shaken vigorously in a machine with 25 cc. of concentrated sulphuric acid (specific gravity 1.84) for 30 minutes. Amount of benzene dissolved, 7 cc., or 28 per cent.

(2) Twenty-five cc. were shaken for 30 minutes with 50 cc. of acid. Amount of benzene dissolved, 18 cc., or 72 per cent.

(3) Twenty-five cc. were shaken for 30 minutes with 75 cc. of acid. Amount of benzene dissolved, 25 cc., or 100 per cent.

The reagents usually employed for removing benzene are a mixture of fuming nitric and concentrated sulphuric acids. The work of Worstall,<sup>1</sup> Francis and Young,<sup>2</sup> and others, shows that such a mixture readily attacks the paraffin hydrocarbons, especially at higher temperatures, forming nitro derivatives, and also oxidizing them to a considerable extent. Furthermore, in working with this mixture the oil must be kept at a low temperature to prevent a violent reaction which results usually in the decomposition of the oil. In this work, therefore, in order to avoid the danger of attacking the paraffin hydrocarbons, and for the sake of convenience, concentrated sulphuric acid was used.

It seems advisable, at this point, to call attention to the fact that the power of ordinary concentrated sulphuric acid to remove benzene and homologous hydrocarbons has been generally overlooked. In order to determine the percentages of these hydrocarbons, it is customary to shake the oils to be analyzed with concentrated sulphuric acid, and then to nitrate the unaffected oil. It is assumed that the acid removes such substances as the unsaturated hydrocarbons, and does not attack the aromatic hydrocarbons. Thus, P.

<sup>1</sup> THIS JOURNAL, 20, 202; 21, 210.

<sup>2</sup> J. Chem. Soc., 1898, 928.



Poni,<sup>1</sup> in determining the presence and percentage of aromatic hydrocarbons in Roumanian petroleum, collected fractions between 35° and 70°, distilled under diminished pressure. These were *purified by shaking with sulphuric acid*, and each nitrated with a mixture of 1 part of nitric acid (specific gravity 1.52) and 2 parts sulphuric acid (specific gravity 1.8). The recovered oils were assumed to be paraffins and naphthenes, while the proportion of benzene and unsaturated hydrocarbons was calculated from the nitro products obtained. It is obvious from the results obtained in the present work that some of the benzene was removed in the process of purifying the fractions. The amount dissolved would depend upon the vigor of the shaking and its duration, as well as on the strength of the sulphuric acid. It is highly probable, therefore, that his percentage of benzene is too low.

In the study of the mixture of benzene and paraffin hydrocarbons, twenty-five cc. of each fraction, or the whole fraction when it was less than 25 cc., were shaken vigorously with three times their volume of concentrated sulphuric acid for 30 minutes. The amount unabsorbed was measured over the acid in a burette, after sufficient time was allowed for most of the oil that was mechanically held in suspension to rise. The oil was then reshaken with a little more acid 15 minutes longer, and the volume again read. In cases where the benzene was present only in small quantities one shaking was sufficient, in other cases it was repeated a second time.

The paraffin oil employed, specific gravity 0.797, was shaken several times with fresh portions of concentrated sulphuric acid until the acid was no longer colored, and only a slight diminution in volume occurred when a small sample of the oil was thoroughly shaken in a machine for some time with the acid. The oil was then washed with water and sodium hydroxide and dried over calcium chloride. The specific gravity decreased to 0.792.

When this oil was mixed with benzene in various propor-

<sup>1</sup> Ann. Sci. Univ. Jassy, **1907**, 192-202 (abstracted in J. Chem. Soc., **92**, II, 883 (1907)).



tions, and allowed to diffuse upward through fuller's earth, the following results, arranged in series, were obtained:

Table III.

Series 1.—Oil alone. Specific gravity 0.792 Level of oil, 28 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene. <sup>2</sup>
A	11	0.789	....	....
B	17	0.792	....	....
C	60	0.7912	0.0154	....
D	100	0.7915	0.0140	....
E	150	0.7913	0.0134	....
F	139	0.7915	0.0134	....

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Orig. vol.,  $\begin{matrix} 477^1 \\ 778 \end{matrix}$

Series 2.—90 per cent. oil (0.792)—10 per cent. benzene (0.8775). Specific gravity, 0.7983. Level of oil, 22 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	11	0.787	....	10.0
B	16	0.7923	....	13.3
C	56	0.7935	0.0131	11.6
D	109	0.7943	0.0123	14.8
E	145	0.7957	0.0120	14.4
F	245	0.7955	0.0116	14.8

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Orig. vol.,  $\begin{matrix} 582 \\ 872 \end{matrix}$

The results that are tabulated in the various series are expressed diagrammatically in the following curves. The ordinates represent the different grades of oil, and the abscissas, the percentages of benzene and the specific gravities.

<sup>1</sup> The original volumes of solution vary with each series, owing to the fact that more or less always remained behind in the reservoir below the level of the tin support. In Series 1, 2, 3, and 4, 950 cc. were supplied to each reservoir; in the rest of the series, each reservoir contained originally 1,000 cc.

<sup>2</sup> In this series the percentages of benzene are not given, because the paraffin oil alone was used,

The final curve represents *in toto* the results of the experimental work upon the diffusion of benzene in solution through fuller's earth. The ordinates of this curve represent the percentages of benzene, and the abscissas, the various mixtures of benzene and oil that were allowed to diffuse through the earth.

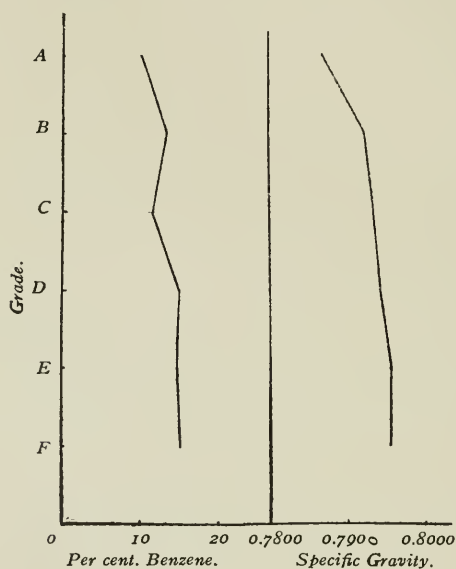


Fig II. Series 2.

Series 3.—80 per cent. oil (0.792)—20 per cent. benzene (0.8775).  
Specific gravity, 0.806. Level of oil, 25 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	25	0.7948	0.0147	15.3
B	35	0.7981	0.0130	16.0
C	78	0.8017	0.0117	22.4
D	126	0.8005	0.0105	21.6
E	166	0.801	0.0107	22.4
F	146	0.798	0.0110	20.8
	576			
Orig. vol.,	892			

Series 4.—75 per cent. oil (0.792)—25 per cent. benzene (0.8775).  
Specific gravity, 0.810. Level of oil, 33 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity. <sup>1</sup>	Per cent. benzene.
A	16	0.800	...	22.0
B	35	0.803	0.0129	23.3
C	74	0.8077	0.0126	24.0
D	128	0.805	0.0114	24.0
E	152	0.8068	0.0102	26.0
F	120	0.8065	0.0105	28.0

Orig. vol., 525  
655

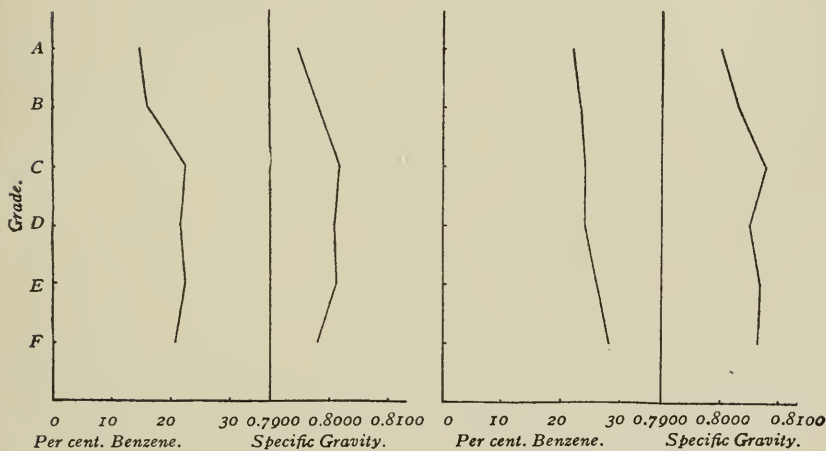


Fig. III. Series 3.

Fig. IV. Series 4.

Series 5.—75 per cent. oil (0.794)<sup>2</sup>—25 per cent. benzene (0.8775). Specific gravity, 0.8115. Level of oil, 24 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	25	0.7942	0.0123	14.0
B	28	0.8048	0.0104	21.2
C	70	0.8105	0.0094	31.2
D	140	0.8100	0.0094	27.6
E	172	0.8100	0.0094	32.0
F	144	0.8093	0.0095	27.6

Orig. vol., 579  
875

<sup>1</sup> The viscosities of Grades A and B in a few of the tables are not given, because, in these series, which were the first to be made, the decision to determine the viscosities was reached only after the fractions had been treated with acid. Since A and B were small, all the oil was used up in this treatment.

<sup>2</sup> In Series 5, 8, 9 and 10 the specific gravity of the refined oil is 0.794. Since the quantity of oil of specific gravity 0.792 was not sufficient for all the series, a second quantity was prepared which had the specific gravity 0.794. This oil was used in the above-mentioned series.

Series 6.—75 per cent. oil (0.792)—25 per cent. benzene (0.8775).  
Specific gravity, 0.8083. Level of oil, 27 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	22	0.7995	0.0106	17.5
B	32	0.8055	0.0099	24.4
C	82	0.8052	0.0100	24.0
D	155	0.8085	0.0093	28.8
E	190	0.8085	0.0093	31.2
F	93	0.8063	0.0096	28.8

Orig. vol., 574  
923

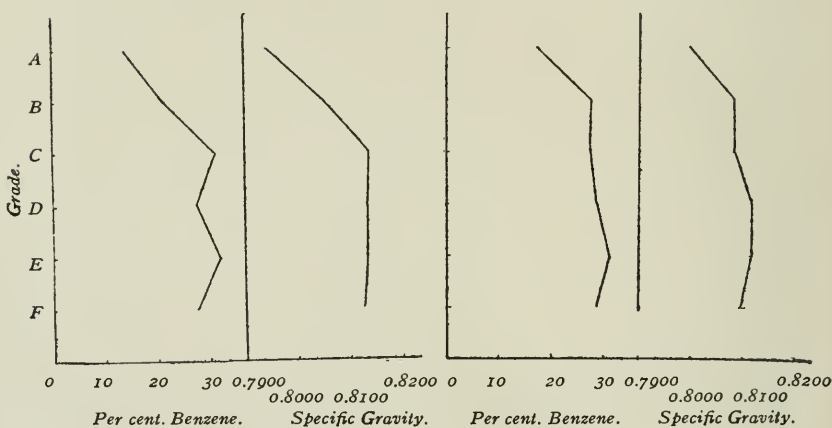


Fig. V. Series 5.

Fig. VI. Series 6.

Series 7.—59.5 per cent. oil (0.792)—40.5 per cent. benzene (0.8775). Specific gravity, 0.8223. Level of oil, 9 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	9 <sup>1</sup>	....	....	....
B	15	0.8069	....	14.0
C	48	0.816	0.0103	22.4
D	96	0.8182	0.0086	31.2
E	160	0.820	0.0082	31.6
F	255	0.8185	0.0083	29.6

Orig. vol., 583  
922

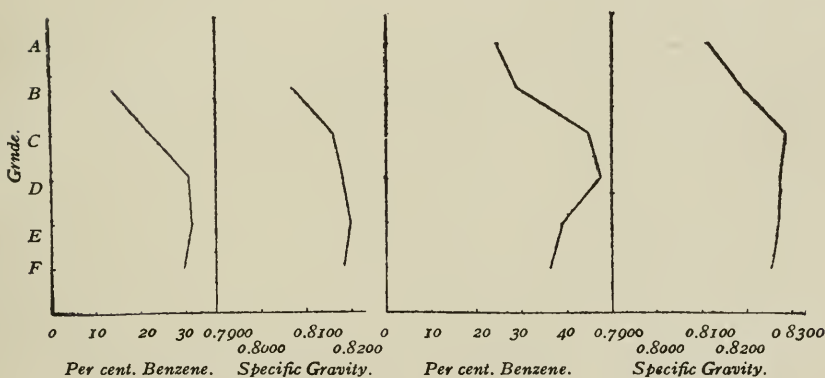
<sup>1</sup> In Series 7 the volume of Grade A recovered was so small that no measurements could be made.

Series 8.—50 per cent. oil (0.794)—50 per cent. benzene (0.8775).

Specific gravity, 0.8295. Level of oil, 17 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	22	0.8122	....	24.5
B	32	0.819	....	28.4
C	78	0.8287	0.0077	44.8
D	111	0.8275	0.0077	47.6
E	155	0.827	0.0077	39.2
F	192	0.8256	0.0079	36.4

Orig. vol., 590  
960



Series 9.—50 per cent. oil (0.794)—50 per cent. benzene (0.8775).

Specific gravity, 0.8315. Level of oil, 18 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	18	0.816	0.0091	26.0
B	24	0.8210	0.0085	34.5
C	76	0.8275	0.0078	47.6
D	136	0.8283	0.0077	50.0
E	174	0.8293	0.0076	49.2
F	144	0.8277	0.0078	40.0

Orig. vol., 572  
923

Series 10.—50 per cent. oil (0.794)—50 per cent. benzene (0.8775). Specific gravity, 0.8295. Level of oil, 16 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
A	31	0.8135	0.0097	31.6
B	45	0.8251	0.0081	43.6
C	85	0.8290	0.0076	46.4
D	140	0.8280	0.0077	47.6
E	175	0.8285	0.0076	49.6
F	137	0.8272	0.0076	50.0

Orig. vol., 613  
972

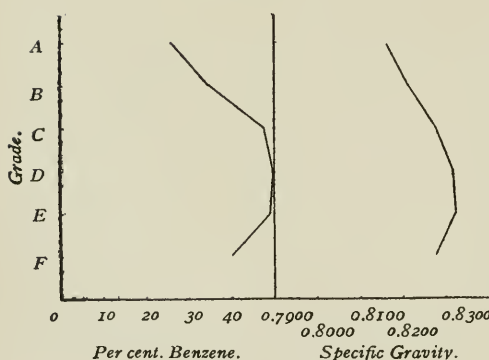


Fig. IX. Series 9.

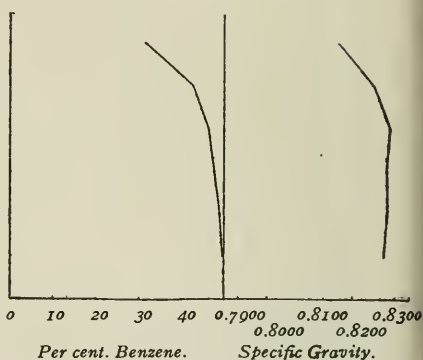


Fig. X. Series 10.

Series 11.—75 per cent. crude oil (0.810)—25 per cent. benzene (0.8775). Specific gravity, 0.8312. Level of oil, 18 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene. <sup>1</sup>
A	12	0.8255	0.0445	....
B	22	0.8268	0.0423	....
C	52	0.8280	0.0300	....
D	76	0.8290	0.0298	....
E	140	0.8300	0.0263	....
F	186	0.8320	0.0276	....

Orig. vol., 488  
890

<sup>1</sup> The percentages of benzene in Series 11, in which crude oil was employed, are not recorded, because, owing to the formation of heavy black emulsions, the loss in volume could not be determined with any degree of accuracy.



Series 12.—Benzene alone (0.8775). Level of oil, 33 cm.

Grade.	Volume of oil, cc.	Specific gravity.	Viscosity.	Per cent. benzene.
<i>A</i>	16	0.8765	....	....
<i>B</i>	15	0.877	....	....
<i>C</i>	68	0.878	0.0066	....
<i>D</i>	128	0.8778	0.0066	....
<i>E</i>	157	0.8775	0.0066	....
<i>F</i>	89	0.8771	0.0066	....

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An examination of these figures shows conclusively that benzene tends to collect in the lower portions of the tube. The specific gravities and viscosities confirm the results obtained by determining the percentages of benzene present by removing the benzene with concentrated sulphuric acid. The specific gravities of Grades *F* to *C* run very close together, and are all much greater than those of Grades *A* and *B*. Since benzene possesses a high specific gravity (in this work the specimen had a specific gravity of 0.8775), the larger value for the lower grades indicates the presence of larger amounts of benzene. The specific gravity of the paraffin oil was only 0.792, showing that the higher specific gravities were due to larger percentages of benzene. Further, since the viscosity of the benzene used was 0.0066, and that of the paraffin oil about 0.0150, the viscosities of those fractions containing higher percentages of benzene, we should expect, ought to be much smaller than those containing less benzene. The results show that the viscosities of the grades *F* to *C* are much smaller than those of *A* and *B*.

It will be observed that the maximum in specific gravity is reached, not at *F*, as might be expected in the fractionation of the crude oil, but between *C* and *D*. Between *B* and *C* there is a marked decrease. This sudden break is found also in the viscosities, and in the percentages of benzene. While the sharp breaks in the curves represent the marked change in the proportion of benzene and the height to which it rises in the tube, no satisfactory explanation has yet been ob-

tained as to why it should occur at these points. This action will be studied more carefully later.

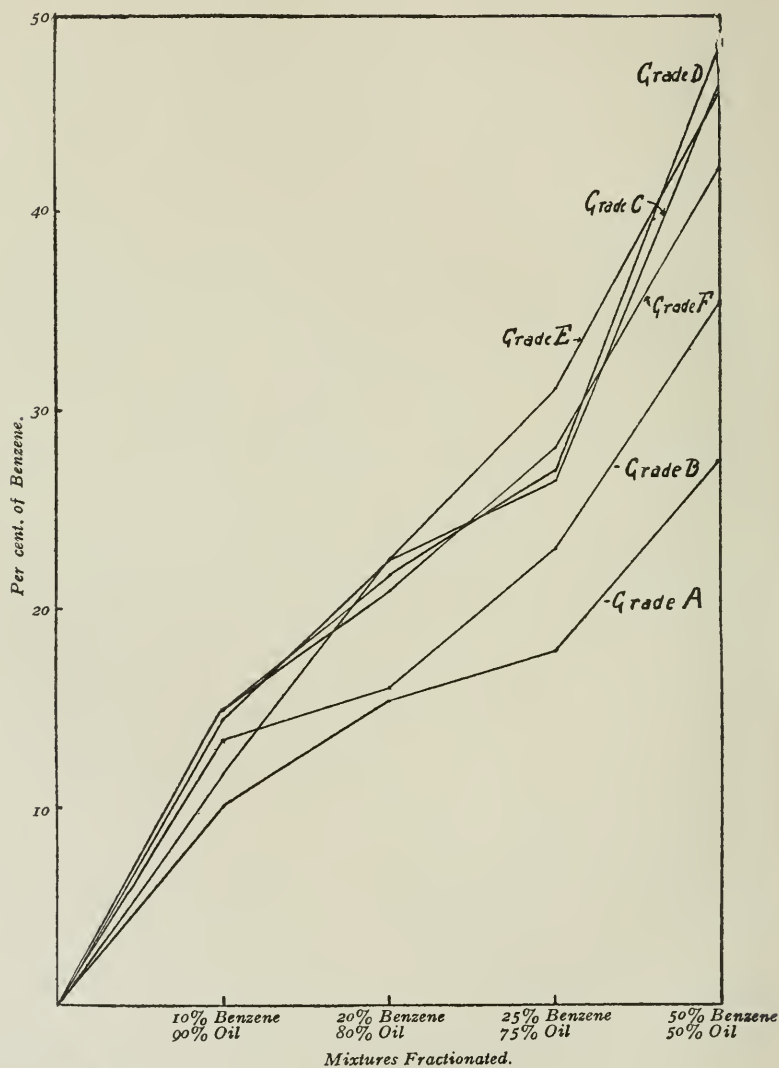


Fig. XI.

In order to determine the degree of exactness of the percentages of benzene obtained, known amounts of benzene were added to the oil until the specific gravity corresponded closely to that obtained by fractionation. The amount of benzene thus added and the amount actually removed by the acid agree very closely, as the following results show:

Benzene in 25 cc. of mixture.    Specific gravity.		Benzene found in the grades of Series 8. cc.    Specific gravity.	
7.3	0.8143	Grade A 7.9	0.8135
9.4	0.8213	" B 10.9	0.8251
11.1	0.8274	" F 12.5	0.8272
11.3	0.8287	" E 12.4	0.8287
11.9	0.8293	" C 11.6	0.8290

The variations in the specific gravities of the mixtures and those of the grade A-F are due to the fact that in the latter series some fractionation had taken place, and therefore the paraffin oils mixed with the benzene were not identical with those mixed with the benzene in the series of prepared mixtures, as the paraffin oil used was not an individual substance but a mixture.

#### *The Fractionation of Crude Petroleum.*

The petroleum employed for the fractionation was an oil obtained from the E. E. Newlin farm, 2.5 miles west of Robinson, Crawford County, Illinois. The specific gravity of the oil was 0.8375 at 20°; its color was dark brown.

The fractionation of the oil was effected by upward diffusion through tubes packed with fuller's earth. In order to shorten the time required for the oil to diffuse by capillarity to the upper parts of the tube, the fine interstices and pores of the earth were evacuated by applying diminished pressure at the top of the tube. By this aid, the time required for the oil to reach the top of a tube was reduced from several weeks to one or two days.

The apparatus employed is the same as that described on page 261.

The tin tubes were packed as uniformly as possible by introducing definite amounts of <sup>77</sup> earth, and ramming solidly

with rods tipped with rubber stoppers. The degree of compactness depended upon the kind of oil to be used. For the crude oil, about one and one-half feet of the tube was filled at a time, and the earth packed as firmly as possible; for the lighter oils, one foot of the tube was filled at a time; for the oils heavier than the crude, between two and three feet of the tube were filled at one time.

The tubes were then placed individually in reservoirs containing 950 cc. of the crude oil, after which diminished pressure was applied at the top of the tubes. The oil rose rapidly at first, then diffused more and more slowly as the tops of the tubes were approached. When the oil in the reservoirs was completely exhausted, the tubes were disconnected from the branched glass tube *F* (see Fig. I) and the oil-laden earth shaken into two breakable cylinders. For the various fractions, the following divisions of the earth were made: Fraction *A* constituted the first 10 cm., measured downward from the level to which the oil had ascended; fraction *B*, the next 15 cm.; *C*, 20 cm.; *D*, 30 cm.; *E*, 35 cm., and *F*, the remainder to the bottom of the tube. In the first fractionation up to Lot 28, fraction *F* was discarded; from Lot 28 to the end of the first fractionation, *E* and *F* were collected together.

After thus dividing the earth, the various portions were placed in separate receptacles and treated with water. After each addition of water the two were thoroughly mixed. The earth, when the oil first appears, is granular; as more water is added, liberating more oil, the earth becomes muddy, and when as much oil as possible has been expelled by the water, the earth has the consistency of glue.

The portions of oil liberated by successive additions of water were collected separately. As Gilpin and Cram<sup>1</sup> pointed out, the oil that is first expelled, if not very small in volume as compared with the oils succeeding, possesses a lower specific gravity than the oil liberated by further additions of water; the latter, in turn, is lighter than the next succeeding oil. The oil that is liberated last, therefore, possesses a higher specific

<sup>1</sup> THIS JOURNAL, 40, 495 (1908).

gravity than any of the oils preceding it. Sometimes, however, the specific gravity remains constant after the second or third extraction. This fractionation, by means of water, was combined with the fractionation effected by the fuller's earth. In the tables that follow,  $A_1$  is the oil first liberated,  $A_2$  the oil next liberated; in the lower fractions, *i. e.*,  $C$ ,  $D$ ,  $E$ , three and sometimes four extractions were made before all the oil that could possibly be liberated by water was recovered.

The specific gravity of the oils was determined by means of the Mohr-Westphal balance. As mentioned before, the fourth decimal is not to be considered as rigidly accurate, but it gives a closer approximation to the truth than if it were entirely discarded. The temperature at which the specific gravity was measured was exactly  $20^\circ$ .

Table IV.—The First Fractionation.

Lot.	1		2		3			
No. of tubes.	15		5		10			
Hours <sup>1</sup> req.	12—14 tubes 23—1 tube		16		17—8 tubes		45—2 tubes	
Frac.	Spec. grav.	Vol., <sup>2</sup> cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
$A_1$	0.8250	312	0.8285	73	0.8223	138	0.8233	50
$A_2$	0.8287	90	0.8310	59	0.8270	54	....	...
$B_1$	0.8367	485	0.8370	218	0.8372	258	0.8405	130
$B_2$	0.8392	250	0.8408	78	0.8400	200	....	...
$C_1$	0.8413	828	0.8440	272	0.8442	290	0.8505	120
$C_2$	0.8460	228	0.8442	136	0.8455	235	0.8535	65
$C_3$	0.8488	126	....	...	0.8480	148	....	...
$D_1$	0.8470	1014	0.8430	313	0.8488	538	0.8546	235
$D_2$	0.8495	375	0.8464	150	0.8500	295	0.8619	30
$D_3$	0.8514	200	0.8500	112	0.8540	115	....	...
$D_4$	0.8555	172	....	...	....	...	....	...
$E_1$	0.8527	720	0.8475	285	0.8537	380	0.8615	172
$E_2$	0.8540	430	0.8509	135	0.8550	245	....	...
$E_3$	0.8570	400	0.8540	118	0.8580	170	....	...

<sup>1</sup> Chapman pump was run day and night. Manometer indicated pressures ranging from 30 to 80 mm.

<sup>2</sup> In lots 1 to 5, 1000 cc. of crude oil were supplied to each tube.

Lot. No. of tubes.	4		5		6			
	10		8		10 <sup>1</sup>			
Hours req.	16		17— 7 tubes 24— 1 tube		17— 1 tube <sup>2</sup> 40— 3 tubes 96— 1 tube		17— 3 tubes 40— 1 tube 150— 1 tube	
	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
Frac.								
A <sub>1</sub>	0.8295	170	0.8313	130	0.8320	72 <sup>3</sup>	0.8287	85 <sup>4</sup>
A <sub>2</sub>	0.8315	100	0.8357	56	0.8352	22	....	...
B <sub>1</sub>	0.8375	327	0.8392	358	0.8405	184	0.8490	134
B <sub>2</sub>	0.8413	250	0.8453	92	0.8451	124	0.8485	35
C <sub>1</sub>	0.8418	505	0.8419	425	0.8443	270	0.8441	218
C <sub>2</sub>	0.8442	223	0.8439	138	0.8495	147	0.8507	67
C <sub>3</sub>	0.8495	74	0.8465	130	....	...	....	...
D <sub>1</sub>	0.8449	495	0.8454	640	0.8483	368	0.8450	302
D <sub>2</sub>	0.8455	328	0.8500	167	0.8517	210	0.8490	132
D <sub>3</sub>	0.8490	260	0.8509	195	....	...	....	...
E <sub>1</sub>	0.8500	545	0.8495	575	0.8500	360	0.8537	215
E <sub>2</sub>	0.8510	295	0.8513	185	0.8569	185	0.8564	174
E <sub>3</sub>	0.8567	170	0.8555	130	....	...	....	....

Lot. No. of tubes.	7				8		9	
	9				10		10	
Hours req.	20— 7 tubes		20— 1 tube 24— 1 tube		19— 8 tubes 22— 2 tubes		24— 2 tubes 40— 8 tubes	
	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
Frac.								
A <sub>1</sub>	0.8325	66	0.8175	45	0.8364	88	0.8215	145
A <sub>2</sub>	0.8356	30	....	...	0.8365	64	0.8234	90
B <sub>1</sub>	0.8395	164	0.8333	110	0.8400	215	0.8330	397
B <sub>2</sub>	0.8418	140	....	...	0.8420	240	0.8350	155
B <sub>3</sub>	....	...	....	...	....	...	0.8400	87
C <sub>1</sub>	0.8408	475	0.8417	132	0.8445	368	0.8415	350
C <sub>2</sub>	0.8468	123	0.8500	22	0.8467	225	0.8436	255
C <sub>3</sub>	....	...	....	...	0.8495	82	0.8480	160 <sup>5</sup>
D <sub>1</sub>	0.8449	500	0.8468	110	0.8465	460	0.8485	507
D <sub>2</sub>	0.8487	270	0.8498	106	0.8478	260	0.8495	280
D <sub>3</sub>	....	...	....	...	0.8500	260	0.8545	247
E <sub>1</sub>	0.8500	483	0.8533	228	0.8490	450	0.8548	313
E <sub>2</sub>	0.8524	318	....	...	0.8495	354	0.8550	275
E <sub>3</sub>	....	...	....	...	0.8521	233	0.8580	375

<sup>1</sup> Beginning with lot 6, 950 cc. of crude oil were supplied to each tube.

<sup>2</sup> The pressure in the tubes was diminished intermittently.

<sup>3</sup> See page 263.

<sup>4</sup> See page 263.

<sup>5</sup> Several cubic centimeters of this fraction were mixed, accidentally, with fraction E<sub>3</sub>.



Lot.	10		11		12		13	
No. of tubes	8		10		9		10	
Hours req.	17		17		42		24— 8 tubes 40— 2 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A <sub>1</sub>	0.8273	130	0.8258	215	0.8325	125	0.8323	122
A <sub>2</sub>	0.8288	75	0.8318	70	0.8345	87	0.8352	96
B <sub>1</sub>	0.8395	220	0.8370	340	0.8430	235	0.8438	245
B <sub>2</sub>	0.8418	160	0.8480	180	0.8467	120	0.8470	180
C <sub>1</sub>	0.8423	240	0.8422	488	0.8470	278	0.8464	317
C <sub>2</sub>	0.8440	195	0.8450	205	0.8487	288	0.8505	235
C <sub>3</sub>	0.8500	150	....	....	....	....	....	....
D <sub>1</sub>	0.8460	410	0.8465	565	0.8495	452	0.8500	312
D <sub>2</sub>	0.8475	210	0.8490	310	0.8522	305	0.8492	375
D <sub>3</sub>	0.8500	348	0.8530	187	....	....	0.8518	150
E <sub>1</sub>	0.8532	320	0.8510	297	0.8505	475	0.8505	450
E <sub>2</sub>	0.8535	282	0.8520	405	0.8533	490	0.8489	395
E <sub>3</sub>	0.8550	215	0.8533	155	....	....	0.8518	180

Lot.	14		15				16	
No. of tubes.	5		6				15	
Hours req.	24 <sup>1</sup>		26— 3 tubes		26— 3 tubes		40— 11 tubes 64— 4 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A <sub>1</sub>	0.8355	132	0.8381	60	0.8305	73	0.8370	200
A <sub>2</sub>	....	....	....	....	....	....	0.8357	108
B <sub>1</sub>	0.8470	236	0.8487	94	0.8452	143	0.8449	490
B <sub>2</sub>	....	....	....	....	....	....	0.8445	226
C <sub>1</sub>	0.8565	98	0.8430	110	0.8465	138	0.8475	635
C <sub>2</sub>	0.8560	150	0.8480	57	0.8509	88	0.8509	235
C <sub>3</sub>	....	....	....	....	....	....	0.8562	90
D <sub>1</sub>	0.8523	170	0.8475	212	0.8505	158	0.8540	825
D <sub>2</sub>	0.8550	205	0.8517	104	0.8522	178	0.8530	495
D <sub>3</sub>	....	....	....	....	....	....	0.8575	150
E <sub>1</sub>	0.8540	150	0.8467	184	0.8561	192	0.8538	775
E <sub>2</sub>	0.8532	325	0.8502	152	0.8585	140	0.8562	620
E <sub>3</sub>	....	....	....	....	....	....	0.8595	205

<sup>1</sup> When the pressure in the tubes was diminished, the oil rose rapidly, and in a short time, the reservoirs were nearly two-thirds exhausted. The pump was stopped, and the remainder of the oil allowed to diffuse during the night under normal pressure.

Lot.	17		18		19		20	
No. of tubes.	9		8		10		10	
Hours req.	40		24— 5 tubes 48— 2 tubes 64— 1 tube		40— 8 tubes 64— 2 tubes		20— 6 tubes 30— 4 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8258	225	0.8322	112	0.8320	146	0.8281	236
B	0.8432	452	0.8435	335	0.8438	385	0.8413	518
C <sub>1</sub>	0.8480	450	0.8495	250	0.8480	300	0.8450	350
C <sub>2</sub>	0.8488	168	0.8500	250	0.8472	315	0.8495	300
D <sub>1</sub>	0.8530	520	0.8530	320	0.8509	422	0.8508	325
D <sub>2</sub>	0.8550	350	0.8540	350	0.8535	355	0.8538	460
E <sub>1</sub>	0.8585	385	0.8547	90 <sup>1</sup>	0.8492	580	0.8513	445
E <sub>2</sub>	0.8598	460	0.8526	640	0.8560	415	0.8540	550
Lot.	21		22		23		24	
No. of tubes.	10		10		10		10	
Hours <sup>2</sup> req.	24— 6 tubes 40— 2 tubes 64— 2 tubes		40— 6 tubes 64— 4 tubes		48— 5 tubes 72— 5 tubes		40— 4 tubes 64— 6 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8275	245	0.8281	210	0.8241	330	0.8250	287
B	0.8410	615	0.8405	508	0.8395	615	0.8408	535
C <sub>1</sub>	0.8452	520	0.8459	265	0.8448	420	0.8463	475
C <sub>2</sub>	0.8488	226	0.8472	410	0.8470	305	0.8505	186
D <sub>1</sub>	0.8512	533	0.8505	435	0.8533	400	0.8540	525
D <sub>2</sub>	0.8535	415	0.8523	450	0.8541	465	0.8540	360
E <sub>1</sub>	0.8557	375	0.8615	385	0.8650	305	0.8623	393
E <sub>2</sub>	0.8625	282	0.8585	365	0.8624	350	0.8645	335
Lot.	25		26		27		28	
No. of tubes.	9		10		10		10	
Hours <sup>2</sup> req.	48— 8 tubes 72— 1 tube		17— 2 tubes 24— 4 tubes 41— 4 tubes		17— 4 tubes 29— 6 tubes		24— 7 tubes 28— 3 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8270	225	0.8284	315	0.8312	230	0.8333	240
B	0.8425	410	0.8422	550	0.8440	470	0.8440	410
C <sub>1</sub>	0.8495	75 <sup>3</sup>	0.8473	520	0.8460	400	0.8458	415
C <sub>2</sub>	0.8492	250	0.8508	178	0.8478	232	0.8500	177
D <sub>1</sub>	0.8509	320	0.8515	600	0.8482	435	0.8470	387
D <sub>2</sub>	0.8510	480	0.8540	230	0.8500	420	0.8498	400
E <sub>1</sub>	0.8556	335	0.8559	490	0.8520	465	0.8492	690 <sup>4</sup>
E <sub>2</sub>	0.8570	395	0.8586	135	0.8565	335	0.8505	600

<sup>1</sup> This irregularity, i. e., the liberation of oil with a specific gravity higher than those of the oils immediately following, is observed when an amount of water is added sufficient to replace a very small amount of oil for the first fraction.

<sup>2</sup> Pressure in the tubes was diminished intermittently.

<sup>3</sup> Some oil of this fraction was lost.

<sup>4</sup> Beginning with lot 28, fractions E and F were collected together.

Lot. No. of tubes. Hours <sup>1</sup> req.	29		30		31		32	
	10		15		10		15	
	18— 5 tubes 40— 5 tubes		20— 7 tubes 41— 6 tubes 63— 2 tubes		44— 4 tubes 89— 6 tubes		40— 7 tubes 89— 4 tubes 103— 4 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8262	300	0.8348	335	0.8292	245	0.8270	445
B	0.8395	505	0.8468	630	0.8439	576	0.8423	726
C <sub>1</sub>	0.8463	390	0.8490	560	0.8495	465	0.8500	730
C <sub>2</sub>	0.8488	270	0.8505	277	0.8523	205	0.8500	220
D <sub>1</sub>	0.8520	510	0.8485	750	0.8517	670	0.8545	750
D <sub>2</sub>	0.8543	290	0.8502	540	0.8552	210	0.8543	540
EF <sub>1</sub>	0.8550	417	0.8520	1125	0.8555	805	0.8580	870
EF <sub>2</sub>	0.8559	645	0.8528	880	0.8610	360	0.8598	910
		<hr/> 3327		<hr/> 5097		<hr/> 3536		<hr/> 5191

Lot. No. of tubes. Hours <sup>1</sup> req.	33		34		35	
	10		10		9	
	41— 4 tubes 65— 4 tubes 89— 2 tubes		44— 6 tubes 68— 4 tubes		48— 6 tubes 72— 3 tubes	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8330	290	0.8355	320	0.8380	235
B <sub>1</sub>	0.8440	365	0.8475	525	0.8460	452
B <sub>2</sub>	0.8462	165	.....	.....	.....	.....
C <sub>1</sub>	0.8502	500	0.8508	470	0.8508	345
C <sub>2</sub>	0.8540	160	0.8543	190	0.8525	245
D <sub>1</sub>	0.8555	655	0.8575	530	0.8549	580
D <sub>2</sub>	0.8562	250	0.8585	325	0.8573	335
EF <sub>1</sub>	0.8575	735	0.8535	895	0.8557	645
EF <sub>2</sub>	0.8585	480	0.8555	405	0.8570	492
		<hr/> 3600		<hr/> 3660		<hr/> 3329

*Observations on the First Fractionation.*

*Specific Gravity.*—The range of the specific gravity extended from 0.8175, the value for Fraction A<sub>1</sub> of Lot 7, to 0.8650, the value for Fraction E<sub>1</sub> of Lot 13. The value for the crude oil itself was 0.8375. The limits of the specific gravities of the individual lots averaged from 0.820 to 0.860. The specific gravity decreases gradually from E to B, but between B and A, the decrease, in most of the lots, is much greater

<sup>1</sup> Pressure in tubes was diminished intermittently.

than between any two consecutive lower fractions. This marked change was also observed in the study of the diffusion of benzene in solution. A detailed investigation into the cause of this sudden divergence will be undertaken in the near future.

*Color.*—The colors of the fractions obtained extended from green to black. The lighter oils possessed a beautiful green fluorescent color, which shaded gradually to brown, and then to the deep black of the heavier oils.

*Odor.*—The unpleasant odor of the crude petroleum disappeared almost entirely in the oils of Fraction A and B; but the other fractions still possessed to a greater or less extent the odor of the natural oil.

*The Volume of Oil Retained by the Fuller's Earth.*—The amount of oil retained by the earth averaged about 55 per cent. of the amount supplied. In the first fractionation of the crude Pennsylvania oil, specific gravity 0.810, Gilpin and Cram found that approximately 40 per cent. of the oil was retained by the earth. It is evident, therefore, that the amount of oil remaining in the earth depends chiefly upon the character of the oil. The Pennsylvania petroleum contains a much smaller percentage of unsaturated hydrocarbons, sulphur, and asphaltic substances than the Illinois oil employed in this investigation. Since the fuller's earth, as will be shown later, readily removes these substances in the process of fractionation, the large percentage of Illinois oil retained by the earth is thus clearly explained. It is safe to conclude that if the heavy Texas or California oil were allowed to diffuse through fuller's earth, the amount of oil retained would exceed the amounts of either of the above-mentioned oils lost in the earth.

#### *The Second Fractionation.*

The products obtained from the first fractionation were united according to the following arrangement:

Lot.	Specific gravity of the oils united.	Specific gravity of mixture.
36	0.8250-0.8350	0.8293
37	0.8350 0.8400	0.8390
38	0.8400-0.8450	0.8433
39	0.8400-0.8450	0.8433
40	0.8450-0.8500	0.8490
41	" "	"
42	" "	"
43	" "	"
44	0.8500-0.8600	0.8543
45	" "	"
46	" "	"
47	" "	"
48	" "	"
49	" "	"
50	" "	"

The oils thus combined were subjected to chilling and filtration for the purpose of removing as much dissolved paraffin as possible. The procedure was as follows: The oils were first chilled at temperatures ranging from 0° to 10° and then filtered through plaited filter papers. When the oil ceased to drip from the funnel, the residue upon the filter paper was placed in a larger filter press, and the remaining oil separated by pressure from the paraffin. The filter press was simple in construction. A piston, fitted closely in an iron cylinder, was gradually forced down upon the oil-laden paraffin, which rested upon a membrane of cotton duck fastened between perforated tin supports. The retained oil was forced through the membrane and was collected from the outlet below. The lighter oils deposited very little paraffin; from the heavier ones somewhat more paraffin was separated. Owing to the high viscosity of the heavier oils, the filtration proceeded very slowly. Since too much time was consumed in this process, the paraffin of some of the oils of Fraction *E* was not removed. A slight change in specific gravity occurred in the oils from which the paraffin was removed.

The final specific gravities of the united oils were as follows:

Lot.	Specific gravity.	
36	0.8305	Paraffin removed.
37	0.8415	" "
38	0.8433	Paraffin not removed.
39	0.8455	Paraffin removed.
40	0.8515	" "
41	0.8515	" "
42	0.8515	" "
43	0.8540	" "
44	0.8543	Paraffin not removed.
45	0.8543	" " "
46	0.8543	" " "
47	0.8543	" " "
48	0.8543	" " "
49	0.8557	Paraffin removed.
50	0.8557	" "

When these oils were again allowed to diffuse upward through fuller's earth, the following fractionation was obtained:

Table V.—The Second Fractionation.

Lot.	36		37		38		39	
No. of tubes.	5		4		8		8	
Hours <sup>1</sup> req.	44— 3 tubes 48— 2 tubes		51		48— 7 tubes 64— 1 tube		29— 4 tubes. 45— 3 tubes. 64— 1 tube.	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8272	160	0.8292	135	0.8331	180	0.8290	255
B <sub>1</sub>	0.8315	216	0.8421	215	0.8447	175	0.8432	355
B <sub>2</sub>	0.8331	58	...	...	0.8455	210	0.8458	110
C <sub>1</sub>	0.8334	350	0.8467	295	0.8490	305	0.8492	455
C <sub>2</sub>	0.8355	85	...	...	0.8505	175	0.8513	180
D <sub>1</sub>	0.8330	360	0.8468	340	0.8492	400	0.8505	740
D <sub>2</sub>	0.8339	320	0.8485	152	0.8509	295	0.8527	275
EF <sub>1</sub>	0.8347	720	0.8480	535	0.8508	710	0.8546	1166
EF <sub>2</sub>	0.8356	320	0.8489	215	0.8518	355	0.8560	350
		2589		1887		3886		2805

<sup>1</sup> In this series, as well as those following, the pressure in the tubes was diminished intermittently.



Lot.	40		41		42		43	
No. of tubes.	9		5		5		4	
Hours req.	48—5 tubes 72—4 tubes		40		69		10 days—2 tubes, 17 days—2 tubes.	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8305	380	0.8316	235	0.8325	210	0.8435	65
B <sub>1</sub>	0.8438	515	0.8460	290	0.8487	265	0.8546	115
B <sub>2</sub>	0.8453	155	0.8480	65	0.8515	54	....	...
C <sub>1</sub>	0.8518	600	0.8523	375	0.8540	335	0.8575	200
C <sub>2</sub>	0.8539	170	0.8540	100	0.8567	56	....	...
D <sub>1</sub>	0.8550	685	0.8558	470	0.8572	420	0.8605	220
D <sub>2</sub>	0.8560	330	0.8571	110	0.8582	175	0.8640	50
EF <sub>1</sub>	0.8605	780	0.8620	580	0.8640	675	0.8650	225
EF <sub>2</sub>	0.8620	600	0.8622	320	0.8650	200	0.8615	78
	<hr/> 4215		<hr/> 2545		<hr/> 2420		<hr/> 953	

Lot.	44		45		46		47	
No. of tubes.	3		5		5		5	
Hours req.	48—2 tubes 96—1 tube		66		93		13 days <sup>1</sup>	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8330	85	0.8362	170	0.8332	210	0.8340	145
B <sub>1</sub>	0.8505	175	0.8510	210	0.8480	260	0.8500	275
B <sub>2</sub>	....	...	0.8522	80	0.8505	50	....	...
C <sub>1</sub>	0.8582	155	0.8562	265	0.8554	300	0.8553	320
C <sub>2</sub>	0.8605	65	0.8585	50	0.8567	95	0.8576	50
D <sub>1</sub>	0.8605	195	0.8567	425	0.8600	370	0.8595	430
D <sub>2</sub>	0.8620	120	0.8580	100	0.8613	120	0.8618	70
EF <sub>1</sub>	0.8672	240	0.8659	615	0.8666	610	0.8665	330
EF <sub>2</sub>	0.8680	175	0.8670	150	0.8680	130	0.8670	215
	<hr/> 1210		<hr/> 2065		<hr/> 2145		<hr/> 1835	

<sup>1</sup> Owing to the weakness of the water pressure, the pressure in the tubes was only slightly diminished. The tubes were taken down before the reservoirs were completely exhausted. The distances to which the oil had risen were 35, 25, 30, 20, 10 cm. from the tops of the tubes.

Lot.	48		49		50	
No. of tubes.	5		7		5	
Hours req.	14 days <sup>1</sup>		48		72— 4 tubes. 89— 1 tube.	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8385	125	0.8341	255	0.8320	170
B <sub>1</sub>	0.8530	275	0.8505	395	0.8485	230
B <sub>2</sub>	....	...	0.8520	95	0.8500	70
C <sub>1</sub>	0.8568	320	0.8560	380	0.8565	300
C <sub>2</sub>	0.8586	90	0.8572	230	0.8577	100
D <sub>1</sub>	0.8610	325	0.8620	500	0.8609	480
D <sub>2</sub>	0.8623	115	0.8625	290	0.8626	125
EF <sub>1</sub>	0.8695	330	0.8705	500	0.8685	640
EF <sub>2</sub>	0.8700	80	0.8705	580	0.8700	235
		1660		3225		2350

*Observations on the Second Fractionation.*

*Specific Gravity.*—The range of the specific gravities grows smaller as the oils to be fractionated become lighter, and less complex. Thus, in Lot 36, the range of specific gravity extends from 0.8272, the value for Fraction A, to 0.8356, the value for EF<sub>2</sub>, the difference between them being 0.0084. In Lot 38, the mother oil, of specific gravity 0.8433, yielded fractions whose specific gravities ranged from 0.8331 to 0.8518, amounting to a difference of 0.0187. This fact appears to be general throughout the various lots, and points to the gradual formations of mixtures which will pass through the earth unaltered, just as the fractionation by distillation tends to yield substances with definite boiling points.

*Color.*—The color of the oils in this fractionation shaded from a very light yellow to greenish black.

*Odor.*—The odor of the crude petroleum vanished completely from the oils of this fractionation.

*Volume of Oil Retained by the Earth.*—The oil retained by the earth in this fractionation amounted to approximately

<sup>1</sup> Owing to the weakness of the water pressure, the pressure in the tubes was diminished but slightly during this time. The tubes were taken down before the reservoirs were completely exhausted. The distances to which the oil had risen were 50, 35, 30, 60, 55 cm. from the tops of the tubes.



*Lot 55.—Specific Gravity 0.8485.*

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
37	$D_1$	0.8468	340	37	$EF_2$	0.8489	215
37	$D_2$	0.8485	152	38	$D_1$	0.8492	400
37	$EF_1$	0.8480	535	47	$B_1$	0.8500	275

1917

*Lot 56.—Specific Gravity 0.8508.*

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
50	$B_2$	0.8500	70	45	$B_1$	0.8510	210
49	$B_1$	0.8505	395	39	$C_2$	0.8513	180
44	$B_1$	0.8505	175	42	$B_2$	0.8515	54
46	$B_2$	0.8505	50	40	$C_1$	0.8518	600
38	$C_2$	0.8505	175				

1909

*Lot 57.—Specific Gravity 0.8509.*

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
39	$D_1$	0.8505	740	38	$D_2$	0.8509	295
38	$EF_1$	0.8508	710	38	$EF_2$	0.8518	355

2100

*Lot 58.—Specific Gravity 0.8558.*

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
49	$B_2$	0.8520	95	49	$C_1$	0.8560	380
45	$B_2$	0.8522	80	45	$C_1$	0.8562	265
41	$C_1$	0.8523	375	50	$C_1$	0.8565	300
48	$B_1$	0.8530	275	42	$C_2$	0.8567	56
40	$C_2$	0.8539	170	46	$C_2$	0.8567	95
42	$C_1$	0.8540	335	48	$C_1$	0.8568	320
41	$C_2$	0.8540	100	49	$C_2$	0.8572	230
47	$C_1$	0.8553	320	43	$C_1$	0.8575	200
46	$C_1$	0.8554	300				

3896

*Lot 59.—Specific Gravity 0.8563.*

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
39	$EF_1$	0.8546	1166	41	$D_2$	0.8571	110
40	$D_1$	0.8550	685	42	$D_1$	0.8572	420
41	$D_1$	0.8558	470	45	$D_2$	0.8580	100
39	$EF_2$	0.8560	350	42	$D_2$	0.8582	175
40	$D_2$	0.8560	330	48	$C_2$	0.8586	90
45	$D_1$	0.8567	425	47	$D_1$	0.8595	430

4750

*Lot 60.—Specific Gravity 0.8615.*

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
46	$D_1$	0.8600	370	41	$EF_1$	0.8620	580
49	$EF_1$	0.8605	780	44	$D_2$	0.8620	120
43	$D_1$	0.8605	220	49	$D_1$	0.8620	500
44	$D_1$	0.8605	195	41	$EF_2$	0.8622	320
50	$D_1$	0.8609	480	48	$D_2$	0.8623	115
48	$D_1$	0.8610	325	49	$D_2$	0.8625	290
46	$D_2$	0.8613	120	50	$D_2$	0.8626	125
47	$D_2$	0.8618	70	42	$E_1$	0.8640	675
40	$EF_2$	0.8620	600				
							5880

*Lot 61.—Specific Gravity 0.8680.*

Lot.	Fraction.	Specific gravity.	Volume, cc.	Lot.	Fraction.	Specific gravity.	Volume, cc.
42	$EF_2$	0.8650	200	46	$EF_2$	0.8680	130
43	$EF_1$	0.8650	225	44	$EF_2$	0.8680	175
45	$EF_1$	0.8659	615	50	$EF_1$	0.8685	640
47	$EF_1$	0.8665	330	48	$EF_1$	0.8695	330
46	$EF_1$	0.8666	610	50	$EF_2$	0.8700	235
47	$EF_2$	0.8670	215	49	$EF_1$	0.8705	500
45	$EF_2$	0.8670	150	49	$EF_2$	0.8705	580
44	$EF_1$	0.8672	240				
							4975

The oils thus united were fractionated by fuller's earth again, with the results given in Table VI.

*Table VI.—The Third Fractionation.*

Lot.	51		52		53		54	
No. of tubes.	3 <sup>1</sup>		2		2		2	
Hours req.	60		60		48		48	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8213	92	0.8219	65	0.8266	73	0.8303	66
B	0.8303	185	0.8333	143	0.8431	115	0.8488	115
$C_1$	0.8337	165	0.8375	190	0.8464	175	0.8518	175
$C_2$	0.8345	90	....	...	....	...	....	...
$D_1$	0.8353	210	0.8388	188	0.8468	145	0.8523	160
$D_2$	0.8356	170	0.8393	90	0.8474	115	0.8528	105
$E_1$	0.8366	385	0.8403	175	0.8473	202	0.8530	245
$E_2$	....	...	0.8411	92	0.8488	73	0.8548	60
$F_1$	0.8373	190	0.8431	88	0.8496	170	0.8548	145
		1487			1031			1068
								1091

The tin tubes used in these lots were 1.5 $\frac{7}{8}$  inches in diameter.

Lot.	55		56		57		58	
No. of tubes.	2		2		2		4	
Hours <sup>1</sup> req.	48— 1 tube 72— 1 tube		96		96		72— 3 tubes 90— 1 tube	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8283	58	0.8313	75	0.8336	55	0.8318	170
B	0.8457	100	0.8488	135	0.8491	130	0.8531	260
C <sub>1</sub>	0.8515	155	0.8546	170	0.8528	180	0.8578	205
C <sub>2</sub>	....	....	....	....	....	....	0.8592	105
D <sub>1</sub>	0.8521	220	0.8553	150	0.8551	185	0.8588	205
D <sub>2</sub>	0.8543	50	0.8560	92	0.8573	45	0.8593	340
E <sub>1</sub>	0.8540	270	0.8553	145	0.8568	170	0.8603	325
E <sub>2</sub>	....	....	0.8563	90	0.8588	70	0.8613	170
F	0.8566	180	0.8575	130	0.8611	170	0.8628	275
	1033		987		1005		2055	

Lot.	59		60		61	
No. of tubes.	5		6		5	
Hours req.	72		72		5 days. <sup>2</sup>	
Frac.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.	Spec. grav.	Vol., cc.
A	0.8328	195	0.8343	195	0.8413	...
B	0.8508	340	0.8540	330	0.8601	...
C <sub>1</sub>	0.8578	325	0.8601	290	0.8683	...
C <sub>2</sub>	0.8588	112	0.8618	130	....	...
D <sub>1</sub>	0.8608	490	0.8628	440	0.8709	...
D <sub>2</sub>	0.8623	135	0.8638	85	....	...
E <sub>1</sub>	0.8628	475	0.8664	425	0.8688	...
E <sub>2</sub>	0.8633	155	0.8683	140	....	...
F	0.8673	330	0.8703	310	0.8691	...

#### Observations on the Third Fractionation.

*Specific Gravity.*—The decrease in the range of specific gravity as the oils supplied become lighter is observed in this fractionation as in the preceding ones.

*Color.*—The lightest oils were almost colorless; the heavier oils were dark brown to green.

*Odor.*—Most of the oils possessed an agreeable odor.

*Prolonged Diffusion.*—In Lot 61, the time required for the oils to reach the tops of the tubes was five days. No fractionation, as is evident from an examination of the specific

<sup>1</sup> The pressure in the tubes was diminished intermittently.

<sup>2</sup> See below, this page.



gravities, occurred in the lower parts of the tubes. The heavier oils of fractions *D*, *E*, and *F* were exceedingly viscous.

*Volume of Oil Retained by the Earth.*—The volume of oil retained by the earth in this fractionation amounted to approximately 45 per cent. The increase in the yield of oil indicates, therefore, a process of purification, in which, as will be shown later, such compounds as the unsaturated hydrocarbons are removed.

*The Fourth Fractionation.*

The following fractions obtained from the third fractionation were united for the fourth fractionation:

*Lot 62.—Specific Gravity 0.8298.*

Lot. Fraction.	Specific gravity.	Volume, cc.	Lot. Fraction.	Specific gravity.	Volume, cc.
51 <i>A</i>	0.8213	92	51 <i>B</i>	0.8303	185
52 <i>A</i>	0.8219	65	56 <i>A</i>	0.8313	75
53 <i>A</i>	0.8266	73	58 <i>A</i>	0.8318	170
55 <i>A</i>	0.8283	66	59 <i>A</i>	0.8328	195
54 <i>A</i>	0.8303	58			—
					979

*Lot 63.—Specific Gravity 0.8343.*

Lot. Fraction.	Specific gravity.	Volume, cc.	Lot. Fraction.	Specific gravity.	Volume, cc.
52 <i>B</i>	0.8333	143	51 <i>C</i> <sub>2</sub>	0.8345	90
57 <i>A</i>	0.8336	55	51 <i>D</i> <sub>1</sub>	0.8353	210
51 <i>C</i> <sub>1</sub>	0.8337	185	51 <i>D</i> <sub>2</sub>	0.8356	170
60 <i>A</i>	0.8343	195			—
					1048

*Lot 64.—Specific Gravity 0.8368.*

Lot. Fraction.	Specific gravity.	Volume, cc.	Lot. Fraction.	Specific gravity.	Volume, cc.
51 <i>E</i> <sub>1</sub>	0.8366	388	52 <i>C</i> <sub>1</sub>	0.8375	190
51 <i>F</i>	0.8372	190	52 <i>D</i> <sub>1</sub>	0.8388	188
					—
					956

*Lot 65.—Specific Gravity 0.8430.*

Lot. Fraction.	Specific gravity.	Volume, cc.	Lot. Fraction.	Specific gravity.	Volume, cc.
52 <i>D</i> <sub>2</sub>	0.8393	90	52 <i>F</i>	0.8431	88
52 <i>E</i> <sub>1</sub>	0.8403	175	55 <i>B</i> <sub>1</sub>	0.8457	100
52 <i>E</i> <sub>2</sub>	0.8411	92	53 <i>C</i> <sub>1</sub>	0.8464	175
53 <i>B</i> <sub>1</sub>	0.8431	115	53 <i>D</i> <sub>1</sub>	0.8468	145
					—
					980





When the oils were warmed, this deposit dissolved completely, showing it to be paraffin.

*Chemical Examination of the Fractionated Oils. Unsaturated Hydrocarbons.*

*Action of Concentrated Sulphuric Acid.*—The percentage of volume of oil absorbed by concentrated sulphuric acid (specific gravity 1.84) was determined according to the following procedure: Ten cc. of the oil to be examined were measured into a glass-stoppered bottle, and thirty cc. of concentrated sulphuric acid were added. The mixture was thoroughly shaken in a machine for thirty minutes and then poured into a burette. After allowing sufficient time for any oil that might be mechanically absorbed in the acid to rise to the top, the volume of unabsorbed oil was read directly over the acid. Owing to the formation of heavy emulsions, no attempt was made to neutralize and wash the oil.

The results of the analyses are given in the table below:

Lot.	Fraction.	Per cent. by volume absorbed.	Lot.	Fraction.	Per cent. by volume absorbed.
51	A	2.3	51	D <sub>1</sub>	11.5
51	B	6.1	51	D <sub>2</sub>	12.0
51	C <sub>1</sub>	9.1	51	E	12.5
51	C <sub>2</sub>	10.2	51	F	14.5

*Action of Bromine.*—The method employed for determining the amount of bromine absorbed by the oils was as follows: Between 0.5 and 0.9 of a gram of the oil to be examined was dissolved in 10 to 15 cc. of carbon tetrachloride. Five cc. of a standard solution of bromine in carbon tetrachloride were then introduced, and the solution allowed to remain, with occasional shaking, in a dark place for 30 minutes. Ten cc. of a 10 per cent. solution of potassium iodide were then added, and the amount of iodine liberated determined immediately by titrating with a standard solution of sodium thiosulphate. A few drops of a starch solution were introduced to mark accurately the end of the titration. The amounts of bromine absorbed by addition and substitution were not estimated separately.

The amounts of bromine absorbed, calculated upon the basis of 100 grams of oil, are given in the following table:

*Table VIII.—First Fractionation.*

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
32	A	5.02	32	D	7.87
32	B	6.96	32	E	8.00
32	C	7.40	Crude oil		7.64

*Second Fractionation.*

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
36	A	4.74	36	D <sub>1</sub>	6.81
36	B <sub>1</sub>	5.40	36	D <sub>2</sub>	6.28
36	B <sub>2</sub>	5.66	36	EF <sub>1</sub>	6.49
36	C <sub>1</sub>	5.56	36	EF <sub>2</sub>	7.18
36	C <sub>2</sub>	6.18			

*Third Fractionation.*

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
51	A	3.27	51	D	4.92
51	B	4.36	51	E	4.71
51	C	4.47	51	F	5.36

*Fourth Fractionation.*

Lot.	Fraction.	Per cent. of bromine absorbed.	Lot.	Fraction.	Per cent. of bromine absorbed.
62	A	2.86	62	E	3.73

These results demonstrate conclusively that the unsaturated hydrocarbons tend to collect in the lower sections of a layer of fuller's earth through which the oil is allowed to diffuse. These figures confirm the results obtained by Gilpin and Cram in their work on the Pennsylvania petroleum. In their investigation, distillation by heat was employed in order to obtain fractions that could be readily studied. In this work the relative amounts of the unsaturated hydrocarbons in the various oils were determined directly as they came from the earth.

The percentages by volume of oil absorbed by concentrated sulphuric acid represent only approximately the per-

centages of unsaturated hydrocarbons, since, as was shown previously, any benzene which may have been present in the oils was also removed by the concentrated acid. This fact rendered impossible a quantitative separation of the aromatic from the unsaturated hydrocarbons. Since no other methods, besides nitration and sulphonation, neither of which could be here employed, were available, no results as to the relative amounts of the aromatic hydrocarbons in the various fractions could be obtained.

It is evident from the results of the bromine determinations that, as the fractionation proceeds, the amounts of unsaturated hydrocarbons become smaller and smaller. A comparison of the amounts of bromine absorbed by Fraction A of the first, second, third and fourth fractionations is given below for the purpose of bringing out this point more clearly:

*Per cent. of Bromine Absorbed by Fraction A.*

First fractionation.	Second fractionation.	Third fractionation.	Fourth fractionation.
5.02	4.74	3.27	2.86

*Sulphur Compounds.*—The sulphur in the various oils was determined by the usual method of combustion. For these determinations, the oils obtained from one tube of Lot 6 were employed. The results are given in the following table:

Lot 6 Fraction.	Specific gravity.	Per cent. sulphur.	Lot 6. Fraction.	Specific gravity.	Per cent. sulphur.
A	0.8195	0.04	D	0.8510	0.09
B	0.8362	0.05	E	0.8600	0.16
C	0.8440	Lost			

The percentage of sulphur in the Fractions A, C and E of Lot 51 was also determined. The results were as follows:

*Table X.—Lot 51.*

Fraction.	Per cent. of sulphur.	Fraction.	Per cent. of sulphur.
A	0.003	E	0.006
C	0.040		

These results show that the sulphur tends to collect in the oils in lower sections of the tube. As the fractionation proceeds, the proportion of sulphur becomes smaller. The figures below indicate that as the oil is subjected to repeated fractionations, the sulphur is gradually removed:



*Per cent. of Sulphur.*

First fractionation.	Second fractionation.	Third fractionation.
Fraction A 0.04	....	0.003
Fraction E 0.16	....	0.006
Fraction C ....	0.08	0.040

*Selective Action of Fuller's Earth.*

When the earth, from which as much oil as possible has been extracted by prolonged treatment of water, is dried, and then digested with ether, oils of surprisingly high specific gravity and viscosity are obtained.

In the experiments undertaken to study the selective action of fuller's earth, the procedure was as follows: The earth under examination was thoroughly treated with water until no more oil appeared. This muddy earth of the consistency of thin liquid paste was spread upon porous plates and allowed to dry at room temperature. Several weeks usually elapsed before the earth became completely dry. It was then finely pulverized, and after being thoroughly soaked and shaken with ether the mixture was allowed to remain undisturbed for 24 hours or more. The mixture was then filtered and the dissolved oil recovered by distilling off the ether from the filtrate. The residual earth was then digested with ether for some time by means of an electric stove that completely surrounded the flask. The oil thus extracted was added to the oil first obtained. In several cases the residual earth was treated further with ether in the Soxhlet extractor.

The results of these extractions are given in the following table:

*Table XI.*

Lot.	Fraction.	Specific gravity at 50°.	Lot.	Fraction.	Specific gravity at 50°.
7	A	0.8470	25	A <sub>3</sub>	0.8391
8	A	0.8502	25	B	0.8489
18	A <sub>1</sub>	0.8419	Specific gravity at 20°.		
18	A <sub>2</sub>	0.8400	51	A	0.8368
19	A <sub>1</sub>	0.8495	51	B	0.8473
19	A <sub>2</sub>	0.8495	51	C	0.8491
19	A <sub>3</sub>	0.8600	51	D	0.8568
25	A <sub>1</sub>	0.8363	51	E	0.8518
25	A <sub>2</sub>	0.8381	51	F	0.8553

The specific gravity of none of the oils of the first and second fractionation, extracted with ether, except those of Lot 19, could be determined at 20° C. All were extremely viscous; those of Lot 25 were so viscous at this temperature that they would not flow when the bottles containing them were inclined. The color of the oils ranges from brown to black. The ethereal solutions, however, of many of the oils were very light in color.

It is interesting to compare the specific gravities of the oils extracted with ether with those of the corresponding oils extracted with water. For this purpose, the oils extracted by water and by ether from the earth of Lot 51 are chosen. In the table below, the specific gravities of these oils at the same temperature, *i. e.*, 20°, are given:

Table XII.—Lot 51. Specific Gravity at 20°.

Frac.	Ether.	Water.	Frac.	Ether.	Water.
A	0.8368	0.8213	D	0.8568	0.8353
B	0.8473	0.8303	E	0.8518	0.8366
C	0.8491	0.8337	F	0.8553	0.8373

As the figures above indicate, the specific gravities of oils extracted with ether are much higher than those of the corresponding oils extracted with water. The presence of such heavy and viscous oils in the upper sections of the tube can be explained only by assuming that they were carried to these heights in solution with the lighter oils, and were then removed by the earth. Since such viscous oils are totally unable to diffuse by capillarity to any appreciable extent, it is not probable that their transportation to the upper parts of the tube was effected by capillary diffusion.

*Chemical Examination of the Oils Extracted by Ether—Unsaturated Hydrocarbons.*

*Action of Concentrated Sulphuric Acid.*—The percentage by volume of oil absorbed by concentrated sulphuric acid (specific gravity 1.84) was determined according to the following procedure: Ten cc. of the oil to be examined were measured into a glass-stoppered bottle, and thirty cc. of concentrated sulphuric acid were added. The mixture was thoroughly shaken

in a machine for 30 minutes and then poured into a burette. After allowing sufficient time for any oil that might be mechanically absorbed in the acid to rise to the top, the volume of unabsorbable oil was read directly over the acid. Owing to the formation of heavy emulsions, no attempt was made to neutralize and wash the oil.

The oils selected for examination were those extracted by ether from the earth of Lots 36 and 51.

The results of the analyses are given in the following table:

Table XIII.

Lot.	Fraction.	Oils extracted by ether. Per cent. by volume absorbed.	Oils extracted by water. Per cent. by volume absorbed.	Lot.	Fraction.	Oils extracted by ether. Per cent. by volume absorbed.	Oils extracted by water. Per cent. by volume absorbed.
36	A	24.0	3.0	51	C	17.0	9.1
36	B	37.0	10.4	51	D	16.4	11.5
51	A	7.0	2.3	51	E	16.5	12.5
51	B	11.5	6.1	51	F	18.0	14.5

*Action of Bromine.*—The method employed for determining the amount of bromine absorbed by the oils has already been described (p. 296).

The amounts of bromine absorbed, calculated upon the basis of 100 grams of oil, are given in the table below. The values for the corresponding oils extracted with water are also given for comparison.

Table XIV.

Lot.	Fraction.	Oils extracted by ether. Per cent. of bromine absorbed.	Oils extracted by water. Per cent. of bromine absorbed.	Lot.	Fraction.	Oils extracted by ether. Per cent. of bromine absorbed.	Oils ex- tracted by water. Per cent. of bromine absorbed.
32	A	5.30	5.02	51	B	4.45	4.36
32	B	7.39	6.96	51	C	6.27	5.03
36	A	5.72	4.74	51	D	6.09	4.92
36	B	6.10	5.40	51	E	5.98	4.71
36	C	6.72	5.56	51	F	5.20	5.36
51	A	3.27	3.27				

As these results clearly demonstrate, fuller's earth retains the unsaturated hydrocarbons, thus exercising a selective action.

*Sulphur Compounds.*—The sulphur in the oils obtained by extraction with ether was determined by the usual method of combustion. The results are given in the table below:

Table XV.

Lot. 51.	Oils extracted by ether. Per cent. of sulphur.	Oils extracted by water. Per cent. of sulphur.	Lot 51.	Oils extracted by ether. Per cent. of sulphur.	Oils extracted by water. Per cent. of sulphur.
A	0.004	0.003	D	0.060	...
B	0.011	...	E	0.080	...
C	0.050	0.040	F	0.080	0.006

The selective action of the earth, in regard to the sulphur compounds, is indicated by these results. This fact was also pointed out by Richardson and Wallace. It is very probable that the earth also retains largely the nitrogen compounds in the oil, and may also remove to a greater or less extent the benzene hydrocarbons.

These results seem to furnish evidence in favor of the view that the Illinois oil diffused, at some time in the history, through porous media, which exercised a selective action upon it, removing a large part of the unsaturated and sulphur compounds, and probably the benzene and nitrogen compounds.

## SUMMARY.

1. When a solution of benzene and a paraffin oil is allowed to diffuse upward through a tube packed with fuller's earth, the benzene tends to collect in the lower sections and the paraffin oil in the upper sections of the tube.

2. When crude petroleum diffuses upward through a tube packed with fuller's earth, a fractionation of the oil occurs. The oil that is displaced by water from the earth from the top of the tube possesses a lower specific gravity than the oil obtained from the earth at the bottom of the tube.

3. As the fractionation proceeds, the range of specific gravity covered in succeeding fractionations becomes smaller, indicating a movement towards the production of mixtures which will finally pass through the earth, unaltered.

4. In the fractionation of petroleum by capillary diffusion through fuller's earth, the amounts of unsaturated hydrocar-

bons and sulphur compounds in the resulting fractions increase gradually from the lightest oils at the top to the heavier oils at the bottom of the tube.

5. Fuller's earth tends to retain the unsaturated hydrocarbons and sulphur compounds in petroleum, thus exercising a selective action upon the oil.

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### REVIEW.

FIRST YEAR CHEMISTRY. A Text in Elementary Chemistry for Secondary Schools. By WILHELM SEGERBLOM, A.B., Instructor in Chemistry at the Phillips Exeter Academy. Exeter, N. H.: Exeter Book Publishing Co. 1909. pp. xxv + 410.

This book includes the entire work of a year. In 390 pages it contains 169 experiments, some chemical history, nearly as much theory as the average first-year college manual, and a small amount of chemical fact. Cut out one-half of the experiments and replace them by descriptive text, and we should get a very good college manual, but then the book would be like many others. The originality of this book lies in leaving out the descriptive text.

The author says in the preface: "My object has been to give the student a conception of chemistry from the point of view of the scholar and the thinker, rather than from the point of view of the crammer, *i. e.*, to teach chemistry rather than to teach a text-book."

Brave words! but surely some others who have written books for this purpose are also scholars and thinkers. Then why did they include descriptive chemistry instead of making their books like this? Simply to give a well-balanced course instead of an ill-balanced course. Every one recognizes the predominant value of laboratory work and gives as much of it as possible.

A few words regarding the relations of school to college may seem a digression but are not. With the present just complaints about the length of the course, school—college—professional work, it is essential to avoid overlapping between school and college, an evil very noticeable in chemistry. Many students entering the average first-year college chemical course have studied little or no chemistry, others more and some nearly enough to pass the course. Those who know nothing of chemistry have to work hard; those who half-know it all waste their time to their detriment.

The secondary school should send the boy to college either



entirely without education in chemistry or with enough to pass off the first-year college chemistry by examination at entrance.

The amount of labor and intelligence demanded for the study of Mr. Segerblom's book is fully equal to that required in the average first-year college chemistry course, but owing to his desire to avoid "teaching a text-book" much that is necessary is omitted. As an example take the author's treatment of nitrogen, ammonia, nitric acid and nitrates. There is no mention of nitrogen in animal or vegetable life, no mention of ammonia being a decomposition product of animal or vegetable substances or of coal, no mention of nitrogen or any compound of nitrogen as plant food, no mention of gunpowder or of the presence of nitrogen in explosives.

In brief, Mr. Segerblom's method is such that the student on entering college would need much of the first-year college chemistry and yet would be over-trained in certain directions for that course, while with suitable guidance and the same amount of labor the student could have done this college work in school and passed it off on entering college.

As a matter of fact, Exeter, the reviewer believes, has a two-years' course in chemistry, so that the author could so arrange the second year's course that the two years would form a harmonious whole. The criticism offered would not apply to such a case, but the author offers the text to the public for use in secondary schools, and says nothing in the preface about further school work. The great majority of secondary schools give only one year to chemistry, and the criticism applies to the use of the book in such schools.

E. R.

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ERRATUM.

✓ P. 134, l. 15, 64.60 should be 84.60.



# AMERICAN CHEMICAL JOURNAL

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## THE REACTION BETWEEN ORGANIC MAGNESIUM COMPOUNDS AND UNSATURATED COMPOUNDS CONTAINING ALKOXYL GROUPS.

BY GRACE POTTER REYNOLDS.

In the work on reactions between organic magnesium compounds and unsaturated compounds, a careful study has been made of the effect of hydrocarbon residues in substances that contain the chain  $C : C.C : O$ .<sup>1</sup> As a result it is possible to predict the mode of addition to a substance with any combination of hydrocarbon residues attached to this chain.

The influence of a few other groups has also been studied. Bromocinnamic ester<sup>2</sup> gives products analogous to those obtained from cinnamic ester, the principal effect of the bromine atom being to diminish the tendency toward formation of secondary products. In the reaction with  $\alpha$ -cyanocinnamic ester<sup>3</sup> and benzalmalonic ester,<sup>4</sup> however, the cyanogen and carboxethyl groups in the  $\alpha$  position prevent the replacement of the alkoxyl group, and, consequently, only 1,4-addition products are obtained.

In continuation of this work it was desirable to study the

<sup>1</sup> THIS JOURNAL, **33**, 153; **36**, 529; **38**, 511.

<sup>2</sup> *Ibid.*, **33**, 35.

<sup>3</sup> *Ibid.*, **33**, 333.

<sup>4</sup> *Ibid.*, **34**, 132.

effect of  $\beta$  substituents, other than hydrocarbon residues, on the reaction between unsaturated compounds and organic magnesium compounds. The principal object of this research was to determine the influence of alkoxyl groups on the mode of addition in these reactions. It was convenient to include an investigation as to the possibility of using the Grignard reagent for the study of keto-enol tautomerism.

Methylmagnesium iodide has been successfully used for the quantitative estimation of the hydroxyl group in a large number of compounds; few of these, however, are substances exhibiting keto-enol tautomerism. In the first paper on the quantitative determination of the hydroxyl group by means of the Grignard reagent, Tschugaeff<sup>1</sup> states that a series of tautomeric substances behaved like hydroxyl compounds toward methylmagnesium iodide. Later, in a general quantitative investigation of the action of the Grignard reagent on substances containing "active" hydrogen, Zerewitnoff<sup>2</sup> included a few tautomeric compounds. His results indicated that they reacted as enols. As these results are not conclusive, it seemed desirable to attempt a systematic investigation in order to decide whether methylmagnesium iodide can be used as a reagent for the study of keto-enol desmotropism.

The reagents most frequently used in recent work on this subject are acetyl chloride, acetic anhydride, phenyl isocyanate and tertiary amines.<sup>3</sup> With tertiary amines the reactions take place at a comparatively low temperature, but with acetyl chloride and acetic anhydride it is generally necessary to heat to a high temperature and, sometimes, even in sealed tubes, to bring about a reaction. The Grignard reaction ordinarily takes place instantaneously and at a very low temperature; it seemed possible, therefore, that methylmagnesium iodide might be well adapted to a study of keto-enolization. The results obtained with tautomeric compounds may be summed up as follows:

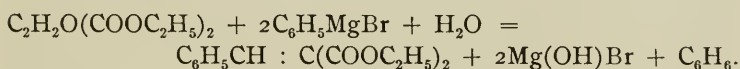
<sup>1</sup> Ber. d. chem. Ges., **35**, 3912.

<sup>2</sup> *Ibid.*, **40**, 2023.

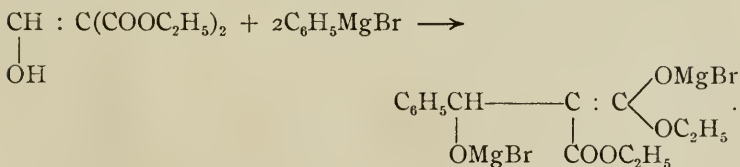
<sup>3</sup> Ann. Chem. (Liebig), **363**, 36.

1. The amount of enolic modification cannot be determined by measuring the volume of methane obtained by treating a known weight of substance with excess of methylmagnesium iodide; when ethyl ether is used as a medium its high vapor tension interferes with the accurate estimation of the gas volume, and when amyl ether is substituted for ethyl ether the reaction goes so slowly that the anticipated advantage of an instantaneous reaction is lost.

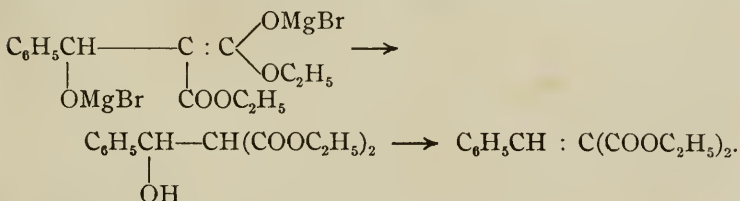
2. The relative amounts of enolic and ketonic modifications cannot be determined by a study of the products obtained when tautomeric substances are treated with the Grignard reagent. This is shown by a consideration of the reaction between phenylmagnesium bromide and the diethyl ester of hydroxymethylenemalonic acid. The sole product of this reaction is benzalmalonic ester, formed by the action of two molecules of the Grignard reagent on one molecule of the ester:



This reaction can be interpreted on the assumption that the ester is an enol, as maintained by Claisen:

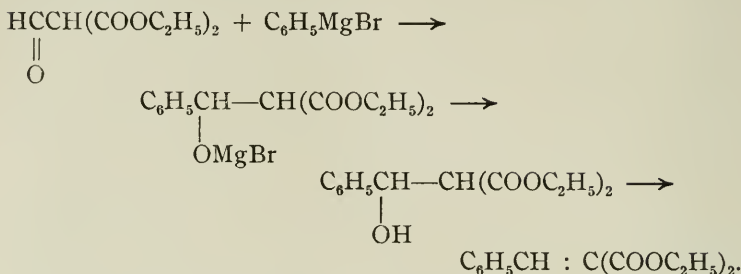


On decomposition, the magnesium derivative would give the diethyl ester of phenylhydroxymethylmalonic acid, and this, by loss of one molecule of water, benzalmalonic ester:



The reaction can be interpreted equally well on the assump-

tion that the ester is an aldehyde, the product being a result of 1,2-addition to carbonyl:

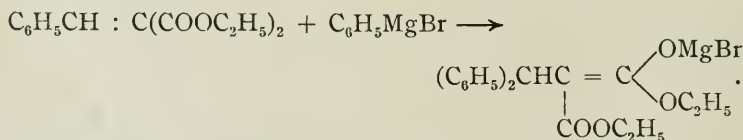


One of these interpretations requires the use of twice as much reagent as the other, but this difference cannot serve as a means of distinguishing between the two, because a large excess is needed in order to have a clean reaction.

These considerations led me to conclude that the Grignard reagent cannot be used for the study of tautomerism.

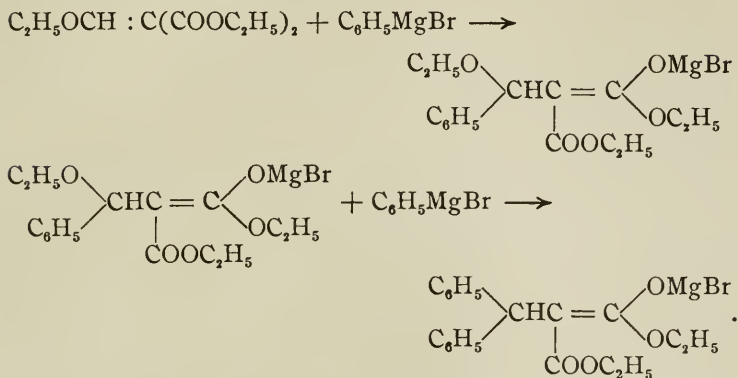
The influence of alkoxyl groups was studied with the diethyl ester of ethoxymethylenemalonic acid. In structure, this substance may be compared with benzalmalonic ester, which differs from it only in having a phenyl group in place of an ethoxyl group. With phenylmagnesium bromide, benzalmalonic ester gives the diethyl ester of  $\beta,\beta$ -diphenylmethylmalonic acid.<sup>1</sup> This is the final product obtained in the reaction between the diethyl ester of ethoxymethylenemalonic acid and phenylmagnesium bromide. In the case of the ethoxy derivative, there are several ways of accounting for the formation of this product.

1. Benzalmalonic ester may be formed by the replacement of the ethoxyl group by a phenyl group; this ester would combine with a second molecule of phenylmagnesium bromide and form the magnesium derivative of  $\beta,\beta$ -diphenylmethylmalonic ester:

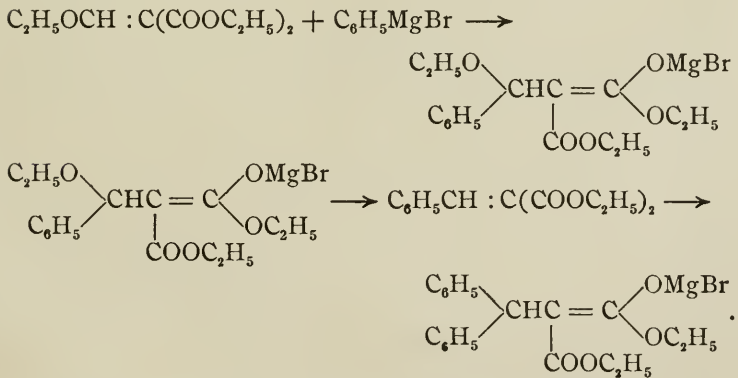


<sup>1</sup> THIS JOURNAL, 34, 132.

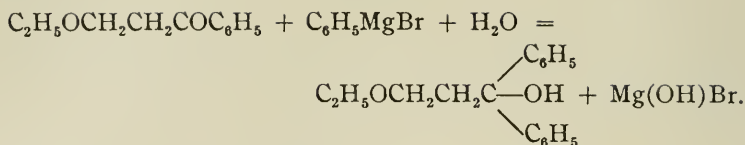
2. The order of the reactions may be reversed and 1,4-addition may take place with subsequent replacement of the ethoxyl group with a phenyl group:



3. Or the mechanism may be represented by the following equations, likewise involving the intermediate formation of benzalmalonic ester:



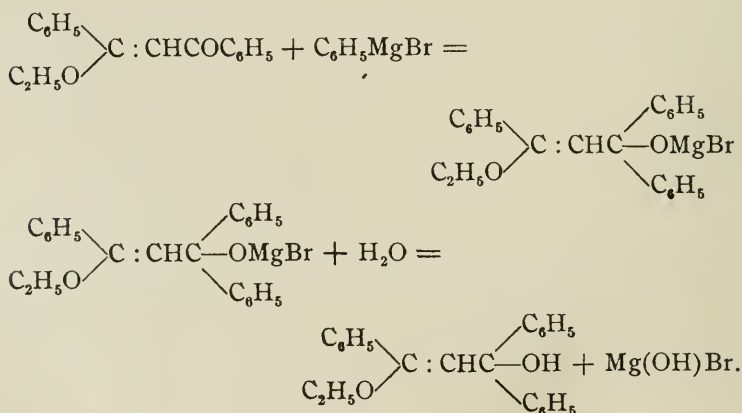
In order to get some evidence as to the mechanism of this reaction,  $\beta$ -ethoxypropiophenone was studied for the purpose of determining whether the ethoxyl group in saturated ketones is replaceable. The ketone gives with both phenylmagnesium bromide and ethylmagnesium bromide solely 1,2-addition products:



This reaction, therefore, is of little assistance in interpreting the action of phenylmagnesium bromide on the ethoxymethylene ester.

More significant are the reactions of  $\beta$ -ethoxybenzalacetophenone which has a phenyl group attached to the same carbon atom that holds the ethoxyl group. The products of the reactions between this ketone and organic magnesium compounds depend upon the concentration of the magnesium compound; in concentrated solution only addition takes place, in dilute solution addition and subsequent replacement of the ethoxyl group. This difference is due to the insolubility of the magnesium derivatives first formed; if a small amount of ether is present these magnesium derivatives appear as white crystalline solids and do not enter into further reaction with the Grignard reagent.

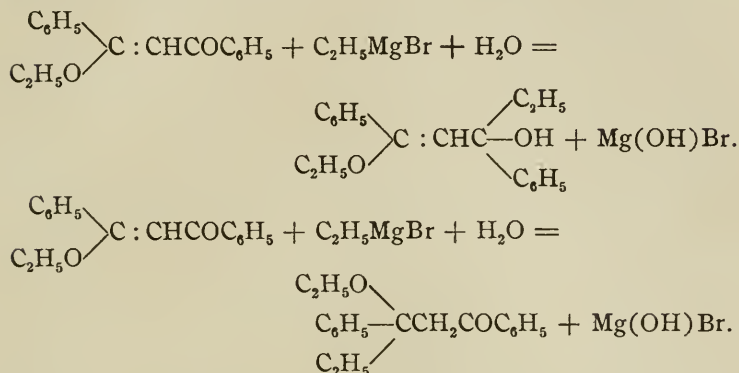
In concentrated solution with phenylmagnesium bromide  $\beta$ -ethoxybenzalacetophenone gives solely a 1,2-addition product:



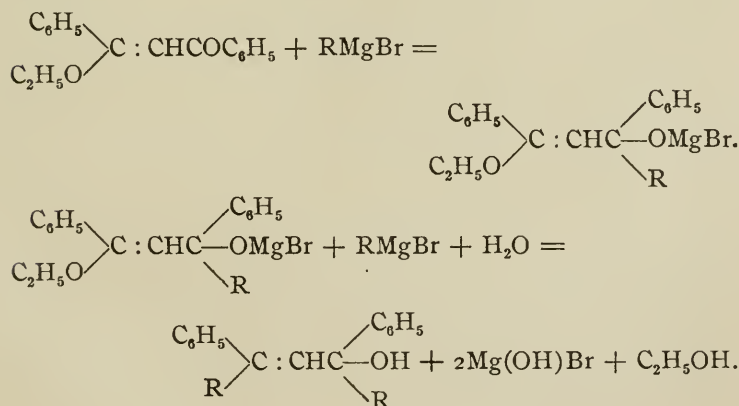
Though with phenylmagnesium bromide 1,2-addition only



takes place, with ethylmagnesium bromide both 1,2- and 1,4-addition products result:



In dilute solution with both phenylmagnesium bromide and ethylmagnesium bromide the ketone, gives 1,2-addition products with a hydrocarbon residue in place of the ethoxyl group:



The study of  $\beta$ -ethoxybenzalacetophenone establishes beyond doubt the mechanism of the reaction between organic magnesium compounds and unsaturated compounds that have an alkoxy group in the  $\beta$  position; the first step is addition, either 1,2 to carbonyl or 1,4 to the conjugated

system; the alkoxyl group of the resulting substance may or may not be replaced later by a hydrocarbon residue.

The influence of the  $\beta$ -ethoxyl group upon the mode of addition in the Grignard reaction is approximately the same as that of the phenyl group. This is shown by the following table in which the amount of 1,4-addition product obtained with  $\beta$ -ethoxybenzalacetophenone is compared with the amount of 1,4-addition product obtained with related ketones. The numbers in Columns 1 and 2 express the percentage of ketone represented by the amount of 1,4-addition product that resulted:

	With $\text{C}_6\text{H}_5\text{MgBr}$ .	With $\text{C}_2\text{H}_5\text{MgBr}$ .
$\text{C}_6\text{H}_5\text{CH} : \text{CHCOC}_6\text{H}_5$	94	99
$\text{CH}_3 \diagup \text{C} : \text{CHCOC}_6\text{H}_5$	mainly	. .
$\text{CH}_3 \diagup \text{C}_6\text{H}_5 \diagdown \text{C} : \text{CHCOC}_6\text{H}_5$	41	44
$\text{CH}_3 \diagup \text{C}_6\text{H}_5 \diagdown \text{C} : \text{CHCOC}_6\text{H}_5$	0	45
$\text{C}_2\text{H}_5\text{O} \diagup \text{C}_6\text{H}_5 \diagdown \text{C} : \text{CHCOC}_6\text{H}_5$	0	18
$\text{C}_6\text{H}_5 \diagup \text{CH}_3 \diagdown \text{C} : \text{CHCOCH}_3$	0	0

#### EXPERIMENTAL.

For the purpose of deciding whether the Grignard reagent can be used for the quantitative estimation of an enolic modification, it seemed best to start with a substance that normally reacts as enol. Accordingly formylethylphenyl ketone was chosen for the investigation. This hydroxymethylene ketone, moreover, is well adapted to the problem because of its comparative stability and because, in the method of procedure adopted, manipulation is less difficult with a solid substance.

#### *Experiments with Formylethylphenyl Ketone.*

Formylethylphenyl ketone was prepared by the method

of Claisen,<sup>1</sup> but the sodium ethylate, used as a condensing agent, was made by suspending sodium wire in absolute ether and adding the calculated amount of absolute alcohol. Difficulty was experienced in obtaining the ketone pure by recrystallization from dilute alcohol as recommended by Claisen. It was purified with the greatest ease, however, by distillation under diminished pressure; boiling point, 155° (25 mm.). The solid, washed with ether to free it of the last trace of coloring matter, was used for the quantitative estimation of an enolic modification.

Hibbert and Sudborough,<sup>2</sup> who developed a method for the quantitative determination of hydroxyl with methylmagnesium iodide, recommended the use of amyl ether as a medium and pyridine as a solvent. These investigators found it necessary to work in an atmosphere of some indifferent gas, owing to the absorption of air by the Grignard reagent. Zerewitnoff, however, found that the method can be used without excluding air from the apparatus.

My method of procedure was essentially that suggested by Zerewitnoff. It was difficult to keep the pyridine dry during the necessary manipulation and also to finish a quantitative determination before an appreciable amount of air was absorbed by the methylmagnesium iodide. Errors in the estimation of the volume of methane due to these experimental difficulties would be opposite in sign and might easily balance each other. Trial reactions with menthol gave results agreeing with those obtained by Zerewitnoff, though a blank test showed that the pyridine was not dry. It was necessary, therefore, to work in an atmosphere of nitrogen if the determinations were to be trusted. In amyl ether the speed of the reaction is very slow. This was shown by the different rates of absorption of air with ethyl ether and amyl ether as media; also by the failure of formylethylphenyl ketone to react with methylmagnesium iodide in the absence of pyridine in amyl ether though the reaction in ethyl ether is instantaneous. This difference in reactivity in the two ethers is

<sup>1</sup> Ber. d. chem. Ges., **22**, 3277.

<sup>2</sup> J. Chem. Soc., **85**, 933.

not due to solubility relations because the ketone is equally insoluble in both of them. These observations showed that this method cannot be used for the quantitative estimation of the hydroxyl group in the hydroxymethylene ketone.

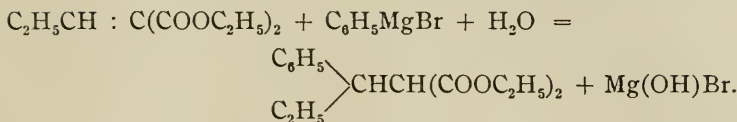
For the purpose of deciding whether the nature of the products obtained in the Grignard reaction can serve for a determination of the relative amounts of ketonic and enolic modifications, it was necessary to use substances with a substituent in the  $\alpha$  position in order to avoid complications owing to secondary reactions. For this study, also, it seemed best to select substances that normally react as enols. The diethyl ester of hydroxymethylenemalononic acid and formylethylphenyl ketone, therefore, were chosen as unsaturated compounds most suitable for this work.

*Experiments with Diethyl Hydroxymethylenemalonate.*<sup>1</sup>

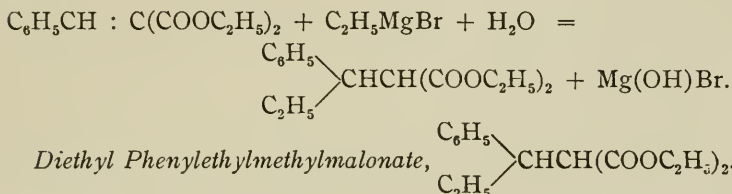
An ethereal solution of this ester was added to an excess of phenylmagnesium bromide. The product was treated in the usual way and fractioned under diminished pressure. A colorless liquid distilled at  $185^{\circ}$  (16 mm.); this is the boiling point of benzalmalononic ester. Since benzalmalononic ester decomposes on hydrolysis, the identity of the product was established by treatment with phenylmagnesium bromide. The saturated ester obtained in this reaction gave, on saponification with alcoholic potassium hydroxide, monoethyl diphenylmethylmalonate, which was identified by comparison with a specimen on hand.

The ester was allowed to react with ethylmagnesium bromide and the product isolated as in the previous case. It boiled at  $117^{\circ}$ – $120^{\circ}$  (14 mm.). Analysis showed that the liquid was impure. As it was impracticable to try to purify it with the small amount of material at my disposal, an indirect method of identification was attempted. If the mode of addition with ethylmagnesium bromide is the same as with phenylmagnesium bromide, the product is propylidenemalononic ester; this would react with phenylmagnesium bromide and form the diethyl ester of phenylethylmethylmalonic acid:

<sup>1</sup> Ann. Chem. (Liebig), **297**, 78.



Since it is very difficult to prepare the hydroxymethylene compound, this saturated ester was made from benzalmalonic ester, which can be procured in quantity with comparative ease:

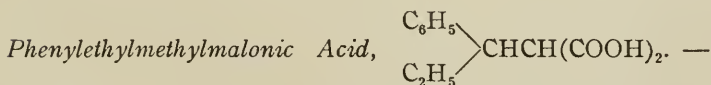


—An ethereal solution of benzalmalonic ester was added to an excess of ethylmagnesium bromide. The magnesium derivative was decomposed in the usual way and the resulting liquid fractioned under diminished pressure. A colorless product distilled at 187°–188° (22 mm.); the yield was quantitative.

Analysis:

0.1727 gram substance gave 0.4370 gram  $\text{CO}_2$  and 0.1144 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{16}\text{H}_{22}\text{O}_4$ .	Found.
C	69.06	69.01
H	7.91	7.36



Strong aqueous potassium hydroxide was added to an alcoholic solution of the ester and the mixture was heated for two hours. On evaporating the alcohol and acidifying the aqueous solution, glistening white plates were precipitated. The acid was purified by recrystallization from warm water. It is very soluble in alcohol, ether and acetone. It crystallizes with one molecule of water and melts at 74°.

Analysis:

0.1122 gram substance lost 0.0083 gram  $\text{H}_2\text{O}$  at  $100^\circ$ .

0.1836 gram substance gave 0.4050 gram  $\text{CO}_2$  and 0.1050 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{12}\text{H}_{14}\text{O}_4 \cdot \text{H}_2\text{O}$ .	Found.
$\text{H}_2\text{O}$	7.50	7.39
C	60.00	60.16
H	6.66	6.35

This acid was shown to be a malonic acid by the product it gave on decomposition. When the dibasic acid was kept at  $150^\circ$  until evolution of carbon dioxide ceased, phenylethyl-

propionic acid,  $\begin{matrix} \text{C}_6\text{H}_5 \\ \text{C}_2\text{H}_5 \end{matrix} \text{CHCH}_2\text{COOH}$ , was obtained. It was purified by recrystallization from ether. It is very soluble in alcohol and ether and melts at  $66^\circ$ .

Analysis:

0.1669 gram substance gave 0.4533 gram  $\text{CO}_2$  and 0.1176 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{11}\text{H}_{14}\text{O}_2$ .	Found.
C	74.15	74.07
H	7.86	7.82

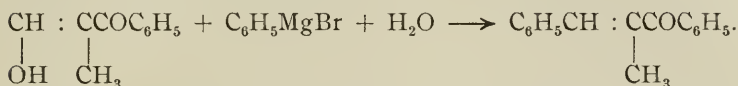
The substance obtained in the reaction between the hydroxymethylene ester and ethylmagnesium bromide was treated with phenylmagnesium bromide. The product was isolated in the usual way and saponified with aqueous potassium hydroxide. An acid was obtained but it could not be made to solidify even by seeding with phenylethylmethylmalonic acid and its identity was not established. It is probable that in the time taken for carrying out the above series of reactions, the product obtained from the hydroxymethylene ester had decomposed to such an extent that it gave a mixture of substances on treatment with phenylmagnesium bromide.

#### *Experiments with Formylethylphenyl Ketone.*

*Reaction with Phenylmagnesium Bromide.*—The solid ketone was allowed to react with phenylmagnesium bromide. The product was treated in the usual way and the resulting sub-



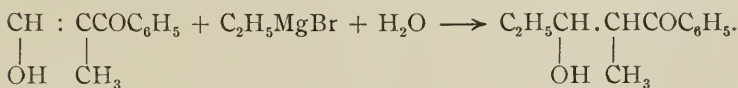
stance fractioned under diminished pressure. A yellow liquid distilled at  $210^{\circ}$ – $213^{\circ}$  (23 mm.), which is the boiling point of benzalpropiofenone.



The substance was identified by its hydrazone, melting at  $127^{\circ}$ – $128^{\circ}$ , and by the product that it gave with phenylmagnesium bromide. The diphenylisobutyrophenone obtained in this reaction was identified by comparison with a specimen on hand.

*Reaction with Ethylmagnesium Bromide.*—Solid hydroxymethylene ketone was added to a solution of ethylmagnesium bromide, the magnesium derivative decomposed in the usual way, and the resulting yellow liquid distilled under diminished pressure. The product boiled at  $137^{\circ}$ – $142^{\circ}$  (16 mm.). As repeated distillations failed to give a pure substance, 100 grams of material were accumulated and subjected to a systematic fractionation, first under diminished pressure and then at atmospheric pressure. The product lost water very gradually when heated to  $130^{\circ}$ , but even after six distillations a cloudy appearance of the distillate indicated that water was still being driven off. It was not practicable, therefore, to eliminate it completely by distillation.

If the mode of addition with ethylmagnesium bromide was the same as with phenylmagnesium bromide, the reaction would be represented as follows:



This saturated ketone, on loss of water, would give propyldenethylphenyl ketone,  $\text{C}_2\text{H}_5\text{CH} : \text{CCOC}_6\text{H}_5$ . An analogous

reaction is the formation of ethyldenacetone from hydracetylacetone.<sup>1</sup> As in this case water was eliminated by

<sup>1</sup> Ann. Chem. (Liebig), 306, 324.

the action of acetic anhydride, the product obtained from the hydroxymethylene ketone was subjected to the same treatment. Analysis of the resulting substance, however, indicated that it was not pure propylidenethylphenyl ketone. That it was this ketone, slightly contaminated by saturated hydroxyl ketone or some material which could not be separated by distillation, was established by two addition reactions.

*Reaction with Bromine.*—The liquid was dissolved in carbon bisulphide, and the solution cooled with a freezing mixture and treated with a solution of bromine in the same solvent. On evaporation of the solvent in a draught the product was left as a solid and was purified by recrystallization from alcohol. The firm, white needles are soluble in ether, acetone and chloroform, less so in methyl alcohol; they melt at 67°.

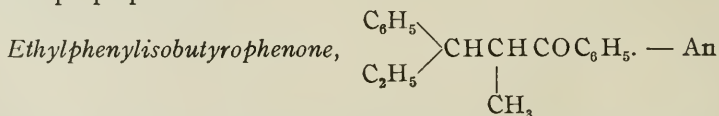
Analysis:

0.1566 gram substance gave 0.2478 gram CO<sub>2</sub> and 0.0585 gram H<sub>2</sub>O.

	Calculated for C <sub>12</sub> H <sub>14</sub> OBr <sub>2</sub> .	Found.
C	43.11	43.15
H	4.19	4.15

As this substance is a dibromide, it proves the presence of an unsaturated ketone, and the excellent yield shows that the liquid is chiefly propylidenethylphenyl ketone.

*Reaction with Phenylmagnesium Bromide.*—For further evidence as to the structure of the product obtained from the action of ethylmagnesium bromide on formylethylphenyl ketone, the reaction between the product and phenylmagnesium bromide was studied. If the substance is chiefly propylidenethylphenyl ketone, it should react with phenylmagnesium bromide and give ethylphenylisobutyrophenone. For purposes of comparison, the ketone was prepared from benzalpropiophenone.



ethereal solution of benzalpropiophenone was added to an excess of ethylmagnesium bromide. On decomposition of

the magnesium derivative a yellow liquid separated and was distilled under diminished pressure. It boiled at  $202^{\circ}$ – $204^{\circ}$  (20 mm.). After several days the liquid deposited crystals, which were purified by dissolving them in methyl alcohol at room temperature and cooling the solution in a freezing mixture. The fine white needles melt at  $60^{\circ}.5$  and are readily soluble in alcohol, ether, acetone and chloroform

Analysis:

0.1591 gram substance gave 0.5018 gram  $\text{CO}_2$  and 0.1136 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{18}\text{H}_{20}\text{O}$ .	Found.
C	85.71	86.01
H	7.93	7.93

The *oxime*,  $\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagup \\ \text{CHCHC} \cdot (\text{:NOH})\text{C}_6\text{H}_5 \\ \diagdown \\ \text{C}_2\text{H}_5 \end{array}$   $\begin{array}{c} | \\ \text{CH}_3 \end{array}$  crystallizes from

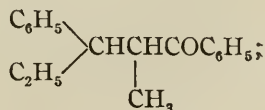
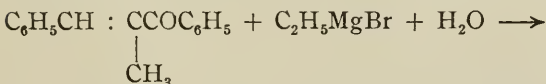
alcohol in heavy, white plates which melt at  $119^{\circ}$ .

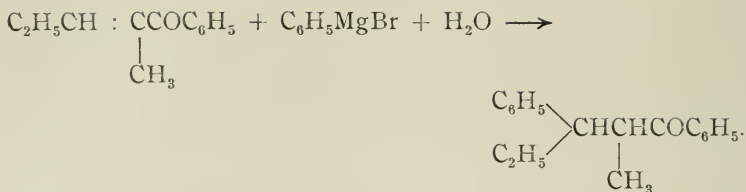
Analysis:

0.1511 gram substance gave 0.4487 gram  $\text{CO}_2$  and 0.1100 gram  $\text{H}_2\text{O}$ .

	Calculated for <del>oxime</del>	Found.
C	80.89	80.98
H	7.86	8.08

The product obtained from the reaction with formylethyl-phenyl ketone, when treated with phenylmagnesium bromide, gave a liquid that boiled at the same temperature as ethyl-phenylisobutyrophenone and solidified in contact with a crystal of this substance. As this solid was identical with that obtained by treating benzalpropiophenone with ethylmagnesium bromide, this established the structure of the unsaturated substance in question.





The two addition reactions show that the product is composed mainly of propylidenethylphenyl ketone. As it readily gave a solid dibromide, an attempt was made to purify it by adding bromine, recrystallizing the resulting solid and then eliminating two bromine atoms with zinc or potassium iodide. Accordingly 60 grams of the liquid were treated with bromine in the same way as before. In this case, however, only a small quantity of solid product could be isolated, though the calculated amount had been obtained from 2 grams of unsaturated ketone. The different result with a large quantity of material might be due to slight variations in the conditions of the reactions; since the dibromketone contains two unequal asymmetric carbon atoms, isomeric products difficult to separate were doubtless formed. The attempt to purify the unsaturated ketone by this method was therefore unsuccessful.

*Experiments with Diethyl Ethoxymethylenemalonate.*<sup>1</sup>

*Reaction with Phenylmagnesium Bromide.*—The ester was allowed to react with phenylmagnesium bromide. On decomposition of the product, a solid substance was obtained and identified as diethyl diphenylmethylmalonate by comparison with a specimen on hand.

*Potassium Ethyl Diphenylmethylmalonate,*

$\begin{array}{c} \text{C}_6\text{H}_5 \\ \text{C}_6\text{H}_5 \end{array} \text{CH} - \text{CH} \begin{array}{c} \text{COOC}_2\text{H}_5 \\ \text{COOK} \end{array}$ .—By treating this ester with alcoholic potassium hydroxide a potassium salt was obtained which was purified by recrystallization from water.

Analysis:

0.1713 gram substance gave 0.0430 gram  $\text{K}_2\text{SO}_4$ .

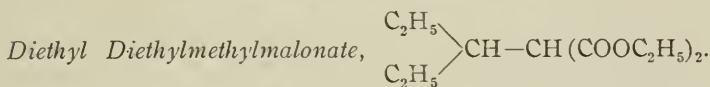
0.1721 gram substance gave 0.0441 gram  $\text{K}_2\text{SO}_4$ .

<sup>1</sup> Ann. Chem. (Liebig), **297**, 75.

	Calculated for $C_{18}H_{17}O_4K$ .	I.	Found.
K	11.60	11.25	11.47

When this salt was acidified, monoethyl diphenylmethylmalonic acid, melting at  $157^\circ$ , resulted. On saponifying the ester with aqueous potassium hydroxide the corresponding dibasic acid was obtained and identified by its melting point,  $190^\circ$ – $192^\circ$  (dip), and by the fact that it lost carbon dioxide at  $175^\circ$  and gave  $\beta,\beta$ -diphenylpropionic acid.

*Reaction with Ethylmagnesium Bromide.*



—From the reaction between the ester and ethylmagnesium bromide a colorless, mobile liquid resulted, which distilled at  $138^\circ$  (21 mm.). Yield, 94 per cent.

*Analysis:*

0.1726 gram substance gave 0.3948 gram  $CO_2$  and 0.1429 gram  $H_2O$ .

	Calculated for $C_{12}H_{22}O_4$ .	Found.
C	62.60	62.38
H	9.56	9.18

*Experiments with  $\beta$ -Ethoxypropiofenone.*

*Preparation.*— $\beta$ -Ethoxypropiofenone has been obtained as a by-product in the preparation of vinylphenyl ketone from dibrompropiofenone. My material was made by the same reaction but by a different procedure since it was necessary to have a product entirely free from unsaturated ketone. Solid dibrom ketone was added in small portions to an alcohol-water solution of potassium iodide. After boiling for two hours the mixture was cooled and poured into an excess of sodium thiosulphate. Steam was passed through the solution, the distillate extracted with ether and the ethereal solution dried with fused sodium sulphate. By removal of the ether and distillation under diminished pressure, 12 grams of  $\beta$ -ethoxypropiofenone were obtained from 33 grams of di-

bromopropiophenone. A test with bromine showed that the product contained no vinylphenyl ketone.

*Reaction with Phenylmagnesium Bromide.*

*Ethoxyethyldiphenylcarbinol*,  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{C} \begin{array}{l} \nearrow \text{C}_6\text{H}_5 \\ \text{— OH} \\ \searrow \text{C}_6\text{H}_5 \end{array}$ . — The

magnesium derivative, formed when the ketone was allowed to react with phenylmagnesium bromide, was decomposed in the usual way and the liquid product distilled under diminished pressure. On cooling, the fraction boiling at  $207^\circ$  (21 mm.) deposited firm, white plates which were soluble in ether, and methyl and ethyl alcohol, and after two recrystallizations from low-boiling ligroin melted at  $78^\circ$ . From 32 grams of ketone 30 grams of product were obtained.

*Analysis:*

0.1578 gram substance gave 0.4611 gram  $\text{CO}_2$  and 0.1061 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{17}\text{H}_{20}\text{O}_2$ .	Found.
C	79.68	79.69
H	7.81	7.47

This substance was shown to be a hydroxyl compound by the Grignard reaction; with ethylmagnesium bromide, ethane was evolved and the original material was regained after decomposition of the magnesium derivative.

An attempt was made to eliminate one molecule of water from ethoxyethyldiphenylcarbinol but the tertiary alcohol was recovered unchanged after being boiled for three hours with excess of acetic anhydride.

*Reaction with Ethylmagnesium Bromide.*

*Ethylethoxyethylphenylcarbinol*,  $\text{C}_2\text{H}_5\text{OCH}_2\text{CH}_2\text{C} \begin{array}{l} \nearrow \text{C}_2\text{H}_5 \\ \text{— OH} \\ \searrow \text{C}_6\text{H}_5 \end{array}$ . — The

product obtained from the reaction between ethoxypropionophenone and ethylmagnesium bromide was a colorless, mobile



liquid boiling at  $151^{\circ}$  (24 mm.). From 33 grams of ketone 28 grams of the product resulted.

Analysis:

0.1700 gram substance gave 0.4700 gram  $\text{CO}_2$  and 0.1453 gram  $\text{H}_2\text{O}$ .

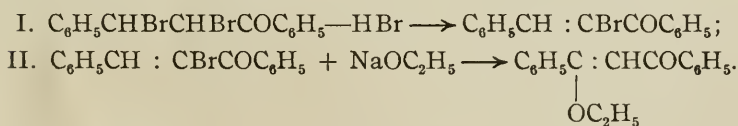
	Calculated for $\text{C}_{13}\text{H}_{20}\text{O}_2$ .	Found.
C	75.00	75.40
H	9.61	9.49

This substance was likewise shown to be a hydroxyl compound by the Grignard reaction.

*Experiments with  $\beta$ -Ethoxybenzalacetophenone.*

*Preparation.*—For the preparation of the large quantities of  $\beta$ -ethoxybenzalacetophenone needed in this work, the methods recommended by Wislicenus<sup>1</sup> and by Ruhemann and Watson<sup>2</sup> were tried, but neither was found satisfactory. The process by which this ketone is formed from dibrombenzalacetophenone is more involved than assumed by these investigators, for Wislicenus regarded the substance as an isomer of dibenzoylmethane and Ruhemann and Watson thought that it could be formed from the corresponding  $\beta$ -brom ketone by direct replacement of bromine with the ethoxyl group.

The reactions by which  $\beta$ -ethoxybenzalacetophenone is formed may be represented by the following equations:



As the first step certainly consists in elimination of hydrobromic acid the procedure of Wislicenus, in which  $\alpha$ -brombenzalacetophenone is first made and subsequently transformed in accordance with equation II, seemed the most promising.

It is easy to remove one molecule of hydrobromic acid,

<sup>1</sup> Ann. Chem. (Liebig), 308, 219.

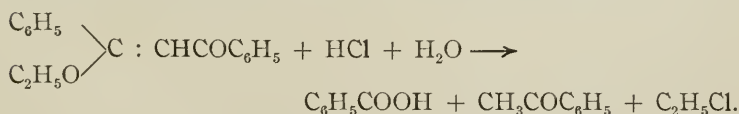
<sup>2</sup> J. Chem. Soc., 85, 456.



when dibrombenzalacetophenone was treated with potassium hydroxide and this method had the additional disadvantage that a large quantity of absolute alcohol was needed.

I found that I could readily get a fair yield of  $\beta$ -ethoxybenzalacetophenone by starting with the dibrom ketone and substituting sodium alcoholate for potassium hydroxide. My method of procedure was as follows: Twenty-six grams of metallic sodium were added to 400 cc. of absolute alcohol. The flask was connected with an inverted condenser and the solution heated to boiling; 210 grams of solid dibrombenzalacetophenone were then added gradually, and the boiling continued for half an hour. The sodium bromide was filtered with suction and washed free of organic material with alcohol. The liquid resulting after removal of the alcohol was fractionated under diminished pressure. It gave 110 grams of a blood-red, viscous product boiling at  $217^{\circ}$  (18 mm.). On dilution with an equal volume of alcohol the liquid deposited solid  $\beta$ -ethoxybenzalacetophenone, which was purified by recrystallization from alcohol. Yield, 70 grams. The filtrate contained a mixture of unsaturated ketone and dibenzoylmethane which was very difficult to separate.

This method of procedure gives no clue as to the mechanism by which  $\beta$ -ethoxybenzalacetophenone is formed. That it has the structure assigned to it, however, was established by Ruhemann and Watson, who heated the ketone in a sealed tube with hydrochloric acid and found that decomposition took place in accordance with the following equation:



*Reaction with Ethylmagnesium Bromide.*—Solid  $\beta$ -ethoxybenzalacetophenone was allowed to react with ethylmagnesium bromide in the usual way. On each addition of ketone a green solid separated, which redissolved immediately and colored the whole solution a brilliant green. The magnesium derivative was decomposed at once with iced hydrochloric acid and the solid product which appeared in the ethereal

layer filtered with suction. On slow evaporation of the ether one gram of another solid separated. This crystallized from alcohol in fine white needles, readily soluble in methyl alcohol, acetone, chloroform and ether, and melting at  $60^{\circ}.5$ .

Analysis:

0.1563 gram substance gave 0.4595 gram  $\text{CO}_2$  and 0.0987 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{19}\text{H}_{22}\text{O}_2$ .	Found.
C	80.85	80.17
H	7.80	7.02

This substance is ethoxydiphenylethylalcohol,  
 $\begin{array}{c} \text{C}_6\text{H}_5 \\ \diagdown \\ \text{C} : \text{CHC} \begin{array}{l} \diagup \text{C}_6\text{H}_5 \\ \text{— OH} \\ \diagdown \text{C}_2\text{H}_5\text{O} \end{array} \end{array}$ . The portion of the product which did not solidify was a colorless, mobile liquid distilling at  $96^{\circ}$  (18 mm.). From 20 grams of ketone there resulted 10 grams of this substance.

Analysis:

0.1569 gram substance gave 0.4654 gram  $\text{CO}_2$  and 0.1022 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{19}\text{H}_{22}\text{O}_2$ .	Found.
C	80.85	80.89
H	7.80	7.23

On treatment of the liquid with semicarbazide hydrochloride and potassium acetate, a solid was deposited in fine, white needles, which, after two recrystallizations from alcohol, melted at  $161^{\circ}$ .

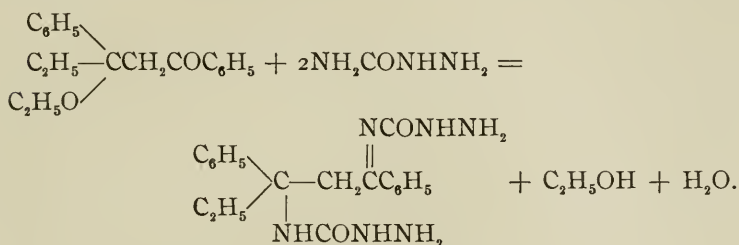
Analysis:

I. 0.1779 gram substance gave 0.4043 gram  $\text{CO}_2$  and 0.1017 gram  $\text{H}_2\text{O}$ .

II. 0.1700 gram substance gave 0.3866 gram  $\text{CO}_2$  and 0.0995 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{19}\text{H}_{24}\text{O}_2\text{N}_6$ .	I.	Found.	II.
C	61.95	61.98		62.02
H	6.52	6.35		6.50

This reaction showed that the liquid product is a ketone; it is ethoxyphenylethylpropiophenone, formed by 1,4-addition of ethylmagnesium bromide to  $\beta$ -ethoxybenzalacetophenone. By the action of two molecules of semicarbazide the semicarbazidesemicarbazone of ethoxyphenylethylpropiophenone was formed, as represented by the following equation:



When the solid product which first appeared after decomposition of the magnesium derivative was digested with chloroform, a very small quantity of a powdery, white substance separated; this, however, was not studied because its extreme insolubility in all ordinary solvents made it difficult to purify. The chloroform solution contained two products, which were separated by fractional crystallization from a mixture of alcohol and chloroform; one formed white needles melting at  $205^\circ$ , the other yellow needles melting at  $185^\circ$ . In solution the white crystals change into the yellow crystals. Combustions and molecular weight determinations indicated that they may be represented by the formula  $\text{C}_{34}\text{H}_{32}\text{O}_3$ .

Analysis:

I. 0.1492 gram substance ( $235^\circ$ ) gave 0.4563 gram  $\text{CO}_2$  and 0.0795 gram  $\text{H}_2\text{O}$ .

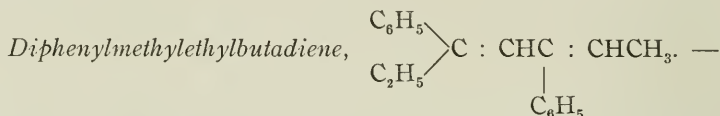
II. 0.1672 gram substance ( $185^\circ$ ) gave 0.5113 gram  $\text{CO}_2$  and 0.0801 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{34}\text{H}_{32}\text{O}_3$ .	I.	Found.	II.
C	83.60	83.40		83.40
H	6.55	5.92		5.32

The molecular weight of the stable yellow product was determined in carbon tetrachloride ( $K = 48.0$ ).

Solvent, grams.	Substance, gram.	Rise of boiling point.	Molecular weight.
95	0.5977	0.07	431
95	1.1200	0.13	435
	Calculated for $C_{34}H_{32}O_3$ ,		488

Since  $\beta$ -ethoxybenzalacetophenone has no substituent in the  $\alpha$  position, it might be expected to give secondary reactions, and these two substances undoubtedly are secondary products. The white crystals change slowly in solution into the yellow crystals. They may be stereoisomers and may result, with elimination of alcohol, by the action of  $\beta$ -ethoxybenzalacetophenone on the 1,4-addition product first formed in the reaction.



When the reaction between ethylmagnesium bromide and  $\beta$ -ethoxybenzalacetophenone was carried out a second time, by chance a much larger quantity of ether was used than in the first experiment. On decomposition of the brilliant green product, the same three high-melting solids previously obtained separated from the ethereal layer, but the portion left after removal of the ether was a colorless liquid boiling at  $191^\circ\text{--}195^\circ$  (20 mm.).

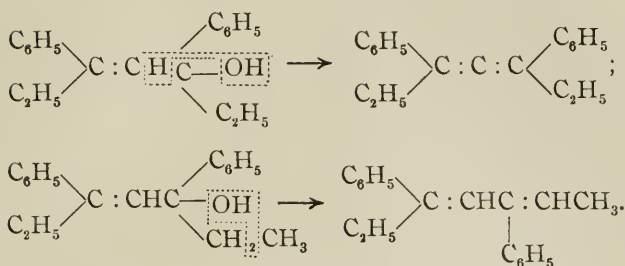
Analysis:

0.1851 gram substance gave 0.6100 gram  $CO_2$  and 0.1340 gram  $H_2O$ .

	Calculated for $C_{19}H_{20}$ .	Found.
C	91.93	89.87
H	8.06	8.04

This analysis indicated an impure hydrocarbon and a test with hydroxylamine showed the presence of ketone. Accordingly the liquid was boiled with hydroxylamine hydrochloride and sodium hydroxide; analysis of the product obtained after this reaction again indicated a hydrocarbon contaminated by some oxygen compound, but it was impossible to separate a pure product by distillation. This substance could be either a butadiene or an allene derivative:





If the substance is diethyldiphenylallene it would be expected to give reactions analogous to those of tetraphenylallene<sup>1</sup> which Vorländer found to be comparatively unreactive. Tetraphenylallene does not decolorize bromine in a freezing mixture nor does it reduce potassium permanganate; the product obtained, however, gives both of these reactions. The liquid was treated with an acetone solution of potassium permanganate, which was reduced rapidly in the cold; the oxidation products isolated were benzoic acid and ethylphenyl ketone. The ketone was identified by its semicarbazone,



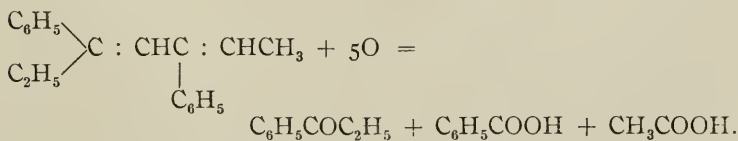
which crystallizes from alcohol in fine white needles melting at 176°.

Analysis:

0.1523 gram substance gave 0.3493 gram CO<sub>2</sub> and 0.0918 gram H<sub>2</sub>O.

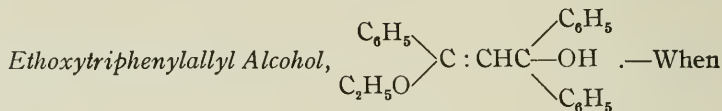
	Calculated for C <sub>10</sub> H <sub>13</sub> ON <sub>3</sub> .	Found.
C	62.82	62.55
H	6.80	6.69

The oxidation reaction, represented by the following equation, establishes beyond doubt that the liquid is a butadiene derivative:



<sup>1</sup> Ber. d. chem. Ges., 39, 1034.

*Reaction with Phenylmagnesium Bromide.*—Solid  $\beta$ -ethoxybenzalacetophenone was added to phenylmagnesium bromide in the presence of a large quantity of ether, as in the second reaction with ethylmagnesium bromide. The Grignard product was decomposed in the usual way and the solid which appeared at once in the ethereal layer was precipitated by addition of low-boiling ligroin. The white crystalline product, which has the melting point,  $139^\circ$ , of tetraphenylallyl alcohol,<sup>1</sup> was identified by treatment with acetic anhydride, which transformed it quantitatively into tetraphenylallene, melting at  $164^\circ$ – $165^\circ$ . The residue left after the removal of the solvent also contained a small quantity of the allene hydrocarbon. Tetraphenylallene was likewise obtained by Vorländer on decomposing the product formed when phenylbenzalacetophenone was treated with phenylmagnesium bromide.



the ketone was allowed to react with phenylmagnesium bromide in the presence of the usual quantity of ether a solid was isolated in the same way as in the last experiment; it crystallized from alcohol in fine, white needles, soluble in acetone, chloroform, ether and methyl alcohol and melting at  $120^\circ.5$ .

Analysis:

0.1490 gram substance gave 0.4566 gram  $\text{CO}_2$  and 0.0812 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{23}\text{H}_{22}\text{O}_2$ .	Found.
C	83.63	83.57
H	6.66	6.05

Reaction with ethylmagnesium bromide showed that this substance is a hydroxyl compound. From 20 grams of ketone 15 grams of ethoxytriphenylallyl alcohol were obtained, but the remainder of the product could not be made to crystallize. As this tertiary alcohol might be expected to lose water, like tetraphenylallyl alcohol, and form an interesting

<sup>1</sup> Ber. d. chem. Ges., **39**, 1026.

allene derivative, both the carefully purified solid and the residue left after removal of the solvents were treated with acetic anhydride. The sole product identified in each case was benzophenone.

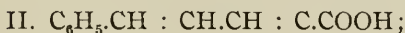
BRYN MAWR COLLEGE,  
May, 1910.

## A COMPARISON OF CERTAIN ACIDS CONTAINING A CONJUGATED SYSTEM OF DOUBLE LINK- AGES.<sup>1</sup>

BY ANNIE LOUISE MACLEOD.

The substituted cinnamylidenacetic acids are of particular interest because they contain the juxtaposed double linkages to which Thiele has given the name of a "conjugated system." Since the character of substances is changed by the introduction of various groups into the  $\alpha$  position to the carboxyl it is possible to use these substituted acids for the purpose of studying the influence of substituents upon the mode of addition to such a conjugated system.

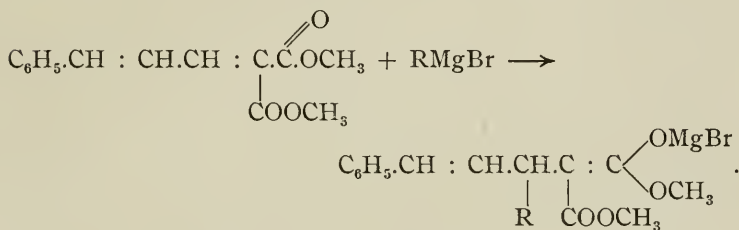
Of the  $\alpha$ -substituted cinnamylidene acids only two have been investigated with any degree of thoroughness, cinnamylidenemalonic acid (I), and  $\alpha$ -phenylcinnamylidenacetic acid (II). For comparison with these I selected  $\alpha$ -methylcinnamylidenacetic acid (III), in which the substituent is more positive, and  $\alpha$ -cyancinnamylidenacetic acid (IV), in which the substituent is more negative than in either of the two acids above mentioned.



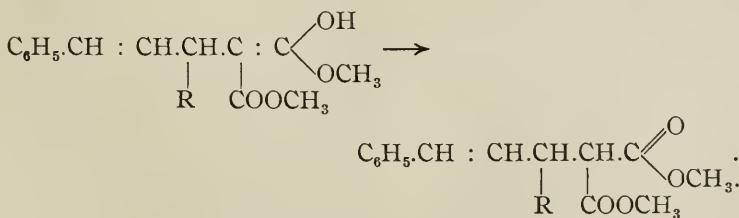
<sup>1</sup> Thesis offered in partial fulfilment of the requirements for the degree of Ph.D. at McGill University.



It is impossible to prove either view to be the correct one in the case under discussion, but the latter would seem the more probable if we reason from the analogous reactions with alkylmagnesium compounds. It has been shown by Reimer<sup>1</sup> that when methyl cinnamylidenemalonate is treated with a Grignard reagent, the magnesium goes to the carbonyl oxygen while the alkyl group goes to the carbon atom which stands in position 4 with regard to this oxygen:

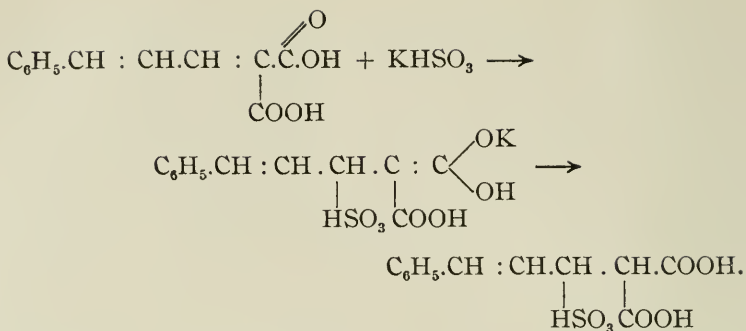


After decomposition, however, the hydrogen by which the magnesium has been replaced is found to occupy the  $\alpha$  position to the carboxyl group, rearrangement having taken place as follows:



As this is the only addition reaction which can be followed step by step, and since in this case a reaction which apparently consists in 1,2-addition to the system  $C : C.C : C$  is found actually to consist in 1,4-addition to the system  $C : C.C : O$ , it seems justifiable, in the absence of any proof to the contrary, to assume the existence of such an intermediate compound in other similar cases, such as the reaction between cinnamylidenemalononic acid and acid potassium sulphite:

<sup>1</sup> THIS JOURNAL, 38, 227.



Under the influence of sunlight cinnamylidenemalonic acid forms a tetramethylene derivative. In this reaction it is the  $\gamma, \delta$  linkage which is involved,<sup>1</sup> as is also the case in the reaction with bromine.<sup>2</sup>

Hinrichsen and Lohse<sup>3</sup> prepared the dibromide of  $\alpha$ -cyan-cinnamylidenacetic acid, and found that with this acid also the bromine goes into the 3,4 position with regard to the carboxyl. A similar constitution has been proved for the dibromide of  $\alpha$ -phenylcinnamylidenacetic acid.<sup>4</sup> As the difference between the mode of addition of hydrocyanic acid, acid sulphites, and similar reagents, and that of hydrogen to cinnamylidenemalonic ester is attributed by Hinrichsen to the fact that in the latter case only the molecule is symmetrical, he attempted to prepare addition products of  $\alpha$ -cyan- and  $\alpha$ -phenylcinnamylidenacetic acids with unsymmetrical reagents, but found that either addition did not take place at all or the product was so unstable that it could not be isolated.

Reimer and Reynolds<sup>5</sup> found that methyl  $\alpha$ -phenylcinnamylidenacetate reacts, though not readily, with magnesium compounds, the product obtained consisting of 87 per cent. ketone formed by replacement of the methoxyl group and addition

<sup>1</sup> Rüber: Ber. d. chem. Ges., **35**, 2411.

<sup>2</sup> Hinrichsen: Ann. Chem. (Liebig), **336**, 200.

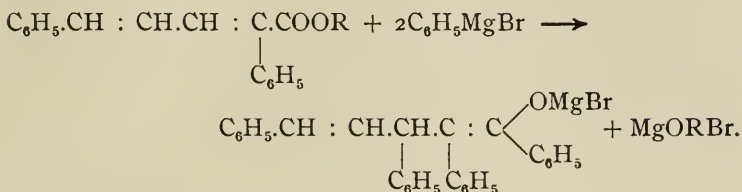
<sup>3</sup> Ann. Chem. (Liebig), **336**, 327.

<sup>4</sup> Hinrichsen: Loc. cit.

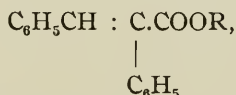
<sup>5</sup> THIS JOURNAL, **40**, 428.



of a second molecule of the magnesium compound in the 1,4 position to the resulting ketone:

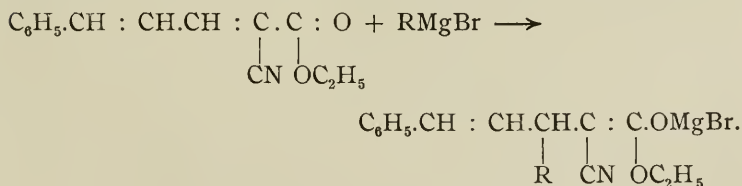


According to these investigators the difference between the behavior of this ester and that of  $\alpha$ -phenylbenzylidenacetate,

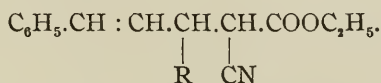


which gives only 1,4-addition product with no replacement of the alkoxyl group,<sup>1</sup> is to be attributed to the spatial arrangement of the molecule.

I have found that the ethyl ester of  $\alpha$ -cyancinnamylidenacetic acid reacts readily with both aliphatic and aromatic magnesium compounds, giving a quantitative yield of the 1,4-addition product. The course of the reaction is as follows:



When this compound is decomposed by water the resulting enol changes to the corresponding ketonic form, so that the final product is the ester

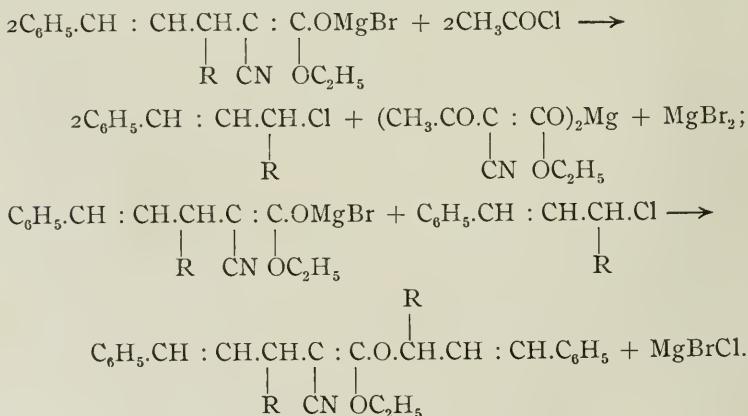


That the magnesium is in combination with carbon, as has been assumed above, and not with the nitrogen of the cyan-

<sup>1</sup> Kohler and Heritage: *THIS JOURNAL*, **43**, 153.

ogen group, as in the reaction with ethyl cyanacetate,<sup>1</sup> follows from the fact that the substance gave no reaction with excess of alkyl halide. Earlier work<sup>2</sup> has shown that 1,4-addition products that have magnesium in combination with nitrogen react with halogen alkyls, giving C-alkyl derivatives, while the magnesium derivatives obtained from esters and ketones do not react at all with simple halogen alkyls. The reaction of  $\alpha$ -cyancinnamylidenacetic ester is therefore similar in every respect to that between  $\alpha$ -cyancinnamic ester and organic magnesium compounds.<sup>3</sup>

As a rule, the magnesium derivatives formed by 1,4-addition behave towards acid chlorides like the metallic derivatives of  $\beta$ -ketonic esters and diketones; the magnesium halide residue is replaced by an acyl group, the product being an *O*-acyl derivative. The only exception heretofore noted is in the case of the magnesium compound obtained from  $\alpha$ -cyancinnamic acid,<sup>4</sup> where the acyl group replaces the diphenylmethyl group, giving the magnesium derivative of a  $\beta$ -ketonic ester, and diphenylchlormethane, which may subsequently react with another molecule of the magnesium compound. A precisely similar reaction takes place with the magnesium derivative of  $\alpha$ -cyancinnamylidenacetic acid:



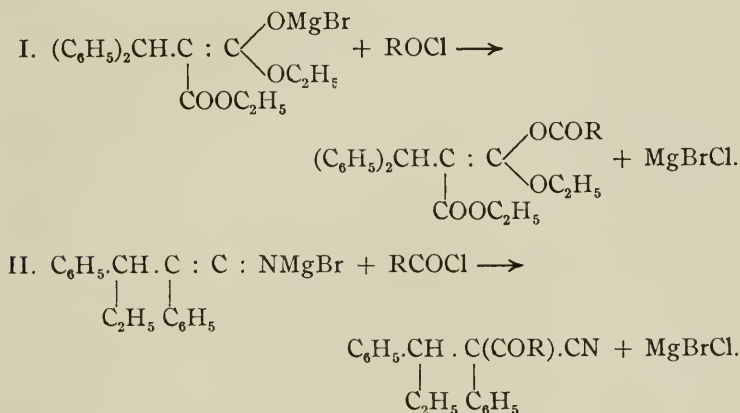
<sup>1</sup> Blaise: *Compt. rend.*, **139**, 674.

<sup>2</sup> Kohler: *THIS JOURNAL*, **35**, 386.

<sup>3</sup> Kohler and Reimer: *Ibid.*, **33**, 333.

<sup>4</sup> Kohler and Reimer: *Loc. cit.*

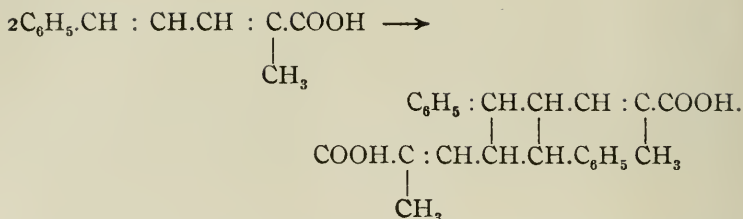
This remarkable reaction depends upon the presence of a cyanogen and an ester group attached to the same carbon atom, as is evident from the fact that it does not take place with the magnesium derivatives of either benzalmalonic ester<sup>1</sup> or  $\alpha$ -phenylcinnamonitrile,<sup>2</sup> the respective reactions in these cases being as follows:



When exposed to sunlight,  $\alpha$ -cyan-,  $\alpha$ -phenyl-, and  $\alpha$ -methylcinnamylidenacetic acids are all decolorized. In the case of the two first mentioned the reaction is extremely slow, so that it was not possible to isolate a definite product. When the  $\alpha$ -cyan acid in a very finely divided state is suspended in water containing hydrochloric acid and exposed to strong sunlight it slowly goes into solution, probably undergoing hydrolysis to the acid amide. The sunlight evidently acts as a catalyst in this reaction, as a similar suspension was kept for months in the dark without any appearance of dissolving. The  $\alpha$ -methyl acid is apparently acted upon by sunlight more rapidly than any other unsaturated acid heretofore observed, the reaction being complete in four days. The product is a tetramethylene derivative corresponding to that obtained from cinnamylidenemalonic acid:

<sup>1</sup> Kohler: *THIS JOURNAL*, **34**, 132.

<sup>2</sup> *Ibid.*, **35**, 386.



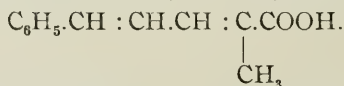
The dimeric acid, like the corresponding substance obtained from cinnamylidenemalonic acid, dissolves in cold concentrated sulphuric acid, giving a pale yellow solution. If the acid is immediately reprecipitated with water it can be recovered unchanged, but if it is left standing overnight in sulphuric acid solution the double molecule is broken down and the monomolecular form is obtained on precipitation. A similar disruption of the double molecule takes place when it is distilled under diminished pressure. This is in accord with Liebermann's observation<sup>1</sup> that  $\alpha$ -truxillic acid changes into cinnamic acid on distillation.

Both  $\alpha$ -cyan- and  $\alpha$ -methylcinnamylidenacetic acids readily react with acid potassium sulphite, giving colorless addition products. These products could not be isolated, however, as they break down, slowly in the cold but rapidly on heating, into their components. The fact that cinnamylidenemalonic acid alone of the  $\alpha$ -substituted cinnamylidene acids gives addition products with acid sulphites which can be isolated probably depends not so much on any greater stability of these products so much as on the fact that they contain a second carboxyl group, by means of which more favorable manipulation is possible.

With bromine  $\alpha$ -methylcinnamylidenacetic acid gives either a di- or tetrabromide according to the conditions of the reaction.

#### EXPERIMENTAL.

##### *Experiments with $\alpha$ -Methylcinnamylidenacetic Acid,*



*Preparation.*—The method first adopted was that described

<sup>1</sup> Ber. d. chem. Ges., **22**, 124.

by Perkin,<sup>1</sup> namely, by heating cinnamic aldehyde, propionic anhydride, and sodium propionate to 160° in a flask fitted with an air condenser. The yield of crude acid obtained in this way amounted to 84 per cent. of the calculated quantity. In later experiments the propionic anhydride was replaced by propionyl chloride and sodium propionate in the proportions necessary for its formation. A mixture of 58 grams sodium propionate and 42 grams cinnamic aldehyde was heated to 160° and 40 grams propionyl chloride added through a dropping funnel at such a rate that the addition occupied from one to two hours. This method gives a somewhat poorer yield (58 per cent. of the calculated quantity), but seems on the whole preferable to that first described on account of the difficulty of obtaining pure propionic anhydride.

The acid obtained by either of these methods is pale yellow, but becomes white on exposure to the light. Perkin makes no mention of this fact, nor does he describe the color of his acid, merely stating that the crystals became opaque on standing. Both forms, and a mixture of the two, have the same melting point, beginning to soften at 158° and melting at 160°–161°.

Analysis:

Yellow acid—0.1680 gram substance gave 0.4718 gram CO<sub>2</sub> and 0.0944 gram H<sub>2</sub>O.

	Calculated for C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> .	Found.
C	76.59	76.59
H	6.38	6.24

White acid—0.1618 gram substance gave 0.4543 gram CO<sub>2</sub> and 0.0940 gram H<sub>2</sub>O.

	Calculated for C <sub>12</sub> H <sub>12</sub> O <sub>2</sub> .	Found.
C	76.59	76.69
H	6.38	6.45

It was of interest to determine whether we have here a case of isomerism, for which there are several possibilities in the structure of this acid, or whether the yellow color is due to

<sup>1</sup> J. Chem. Soc., **31**, 406.

some impurity. The following experiments were undertaken in order to determine this point.

*Crystallization.*—The yellow acid separates from alcoholic solution in thick prisms, the white form in flat, leaflike plates. Neither the melting point nor the crystalline form is affected by repeated crystallization. The yellow color becomes slightly paler, which may be due either to gradual dilution of an impurity present, or to partial transformation of one isomer into another during the process of recrystallization.

*Crystallization of Mixed Acids.*—Equal quantities of yellow and of white acids, each specimen having been carefully purified by recrystallization, were ground up together in a mortar and dissolved in sufficient alcohol to make a fairly dilute solution. Into the cold solution a yellow and a white crystal were introduced at opposite sides of the beaker, and the whole left to crystallize slowly in the dark. Under these conditions the crystals which separated out were of a uniform pale yellow color, and all in the thick prisms characteristic of the yellow acid. At the end of the experiment the original yellow and white crystals each formed the core of a crystalline mass, from which they could readily be distinguished by the color, which was paler in one case, deeper in the other. It is evident, therefore, that if there are two isomeric acids they are capable of crystallizing together in mixed crystals, a phenomenon which is unusual though not unknown in the case of stereoisomers. Klingemann<sup>1</sup> has observed that the two forms of benzylidenedesoxybenzoin behave similarly.

*Purification through Sodium Salt.*—If the yellow acid be dissolved in sodium carbonate solution the salt which crystallizes out is colorless. This salt was ground finely, extracted with ether for eight hours in a Soxhlet apparatus, and recrystallized from water, in which it is very soluble and from which it separates in colorless shining plates. The acid obtained from this salt by precipitating with hydrochloric acid and recrystallizing from alcohol was lemon-yellow. It follows that if the yellow color is due to an impurity this impurity must be an acid substance, since it imparts no color to the

<sup>1</sup> Ann. Chem. (Liebig), **275**, 60.



sodium salt and cannot be extracted from it by organic solvents. No variation could be detected in the color of the resulting acid either by use of a very weak acid, such as carbonic acid, for precipitating from a solution of the sodium salt, or by fractional precipitation by hydrochloric acid.

*Esterification.*—The acid is readily esterified, the reaction being complete on boiling for three hours with a three per cent. solution of hydrochloric acid in methyl alcohol. The products from the yellow and white forms are identical, a well-defined crystalline compound being obtained in each case. This is easily purified by recrystallization from methyl alcohol, in which it is readily soluble, and from which it separates in colorless needles melting at  $87^{\circ}$ .

Analysis:

0.1717 gram substance gave 0.4855 gram  $\text{CO}_2$  and 0.1038 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{13}\text{H}_{14}\text{O}_2$	Found.
C	77.22	77.11
H	6.93	6.75

Molecular weight:

Ether.	Substance.	Difference in boiling point.	Molecular weight.
58.948	0.2010	0.0375	196
	0.4098	0.0700	214
	0.5502	0.0950	212
Calculated for $\text{C}_{13}\text{H}_{14}\text{O}_2$ ,		202.	Average found, 207

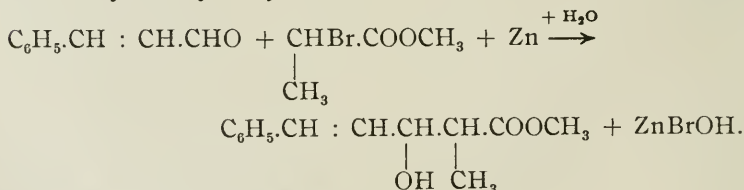
On treating with alcoholic potassium hydroxide the potassium salt separated as small plates on standing at room temperature for a short time, and this, on acidifying, gave a pure white acid which crystallized from alcohol in the characteristic leaflike plates. When the hydrolysis is carried out by boiling with aqueous potassium hydroxide the acid obtained is yellow.

Several cases are known in which esterification of stereoisomeric acids by boiling with three per cent. hydrochloric acid in alcohol results in the formation of the ester corresponding to one form only. Thus maleic acid treated in this manner gives ethyl fumarate. Similarly,  $\beta$ -bromocinnamic acid, under the same conditions, gives the ester of  $\alpha$ -bromocinnamic

acid.<sup>1</sup> Anschütz<sup>2</sup> has shown that in both cases this is due to the transforming influence of the hydrochloric acid and that esterification through the silver salt with alkyl iodide gives the normal product. Accordingly, the silver salts of both the yellow and the white forms were prepared and treated with methyl iodide. The only product obtained was the ester melting at 87°.

When the yellow acid, in cold alcoholic solution, was treated with an amount of sodium amalgam sufficient to neutralize only about 4 per cent. of the acid present the yellow color disappeared, leaving the colorless acid, which crystallized from the alcoholic solution. It follows, therefore, that the substance to which the yellow color is due is present only in small amount. Whether this substance is an isomeric acid or not cannot be proved without further work, but in any case it is evident from the results described that its presence does not affect the reactions which form the specific subject of this investigation. The following experiments were carried out with yellow acid obtained by recrystallizing the crude product until it gave a constant melting point of 160°.

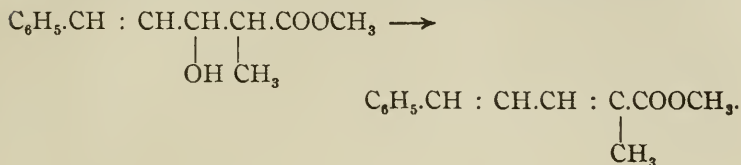
In the course of later experiments it was found that this acid could be more advantageously prepared by making use of the reaction between cinnamic aldehyde and  $\alpha$ -brompropionic ester in the presence of zinc. For this purpose, 21 grams of cinnamic aldehyde, 32.5 grams brompropionic ester, and 13 grams zinc in 100 cc. dry benzene were heated for an hour and a half on the water bath. At the end of this time the solution was poured into dilute hydrochloric acid and extracted with ether. After evaporating the ether the product left was a yellow oil which would not solidify. This was undoubtedly the hydroxy ester formed according to the scheme:



<sup>1</sup> Barisch: J. prakt. Chem., **20**, 182.

<sup>2</sup> Ber. d. chem. Ges., **12**, 2282; **20**, 1382.

On distillation under diminished pressure this ester loses water, giving the ester of  $\alpha$ -methylcinnamylidenacetic acid:



A yield of from 80 to 90 per cent. of the calculated amount of this ester is obtained in this way.

*Effect of Light.*—In order to obtain the acid in the most suitable condition for exposure, 10 grams were dissolved in sodium carbonate solution and made up to about two liters in a large flask. Dilute hydrochloric acid was added slowly until the whole amounted to about four liters. After exposure to bright sunlight for half an hour the suspended acid appeared quite white, but this change was probably only superficial, as the crystals obtained after filtering, drying, and recrystallizing were yellow. After exposure to sunlight for eight hours, with occasional shaking, the acid, after filtering and drying, separated from alcohol in thin plates which were perfectly colorless. There was no appreciable change in melting point after exposure for this length of time.

When the exposure was continued for about four days in direct sunlight the suspended acid was found to have undergone further change. The product was difficultly soluble in alcohol and crystallized from it in small white prisms melting at  $253^\circ$ – $254^\circ$ .

Analysis:

0.1243 gram substance gave 0.3487 gram  $\text{CO}_2$  and 0.0723 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{24}\text{H}_{24}\text{O}_4$ .	Found.
C	76.59	76.35
H	6.38	6.51

*Oxidation.*—The constitution of this high-melting product was determined by oxidation. For this purpose 13.5 grams

of acid, which had been exposed to sunlight for over a week, was dissolved in slight excess of sodium carbonate solution and 53 grams of powdered potassium permanganate added. After standing overnight the oxides of manganese were filtered off and the filtrate acidified with hydrochloric acid. An acid separated, which, after several recrystallizations, first from 50 per cent. alcohol and finally from benzene and ligroin, melted at  $174^{\circ}$ , the melting point of  $\alpha$ -truxillic acid.

Identification with this acid was completed by preparing the dimethyl ester. On saturating a solution of the acid in methyl alcohol with hydrochloric acid a crystalline ester separated which melted at  $174^{\circ}$ .

Analysis:

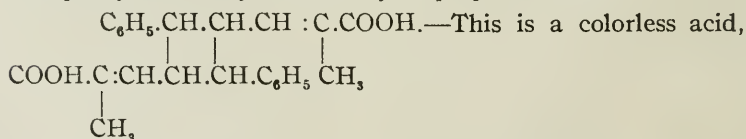
0.2288 gram substance gave 0.6205 gram  $\text{CO}_2$  and 0.1222 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_4$ .	Found.
C	74.07	73.98
H	6.17	5.99

The filtrate from the  $\alpha$ -truxillic acid, on evaporation, deposited benzoic acid, which was recrystallized and identified by its melting point. The filtrate from this was extracted with ether, neutralized with ammonia, and treated with calcium chloride solution. A fine white precipitate separated, which was found to be calcium oxalate.

The products of oxidation are therefore  $\alpha$ -truxillic acid, benzoic acid, and oxalic acid, from which it is evident that the high-melting acid contains a tetramethylene ring. It is a compound analogous to that formed by cinnamylidene-malonic acid in sunlight.<sup>1</sup>

*Diphenyltetramethylenebismethylenepropionic Acid,*



crystallizing in small transparent prisms, melting at  $253^{\circ}$ – $254^{\circ}$ . It is soluble in alcohol and in acetone, and fairly solu-

<sup>1</sup> Riiber: Ber. d. chem. Ges., **35**, 2411.

ble in glacial acetic acid; insoluble in chloroform, benzene, and ether.

*Methyl Diphenyltetramethylenebismethylenepropionate*.—When the acid is boiled with a three per cent. solution of hydrochloric acid in methyl alcohol it gives an ester which crystallizes well from methyl alcohol and melts at  $126^{\circ}.5$ – $127^{\circ}$ .

Analysis:

0.1441 gram substance gave 0.4076 gram  $\text{CO}_2$  and 0.0888 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{26}\text{H}_{28}\text{O}_4$ .	Found.
C	77.22	77.14
H	6.93	6.84

On distilling under a pressure of 32 mm. the acid boiled constantly at  $238^{\circ}$ , the product being a clear yellow substance which, on recrystallization, proved to be pure  $\alpha$ -methylcinnamylidenacetic acid, melting at  $160^{\circ}$ – $161^{\circ}$ .

*Bromine Addition Product*.—When diphenyltetramethylenebismethylenepropionic acid was treated with bromine a solid product was obtained which, on analysis, appeared to be a mixture of dibromide and tetrabromide. The methyl ester, on treatment with bromine in chloroform solution, gives a solid tetrabromide which can be recrystallized from chloroform, in which it is readily soluble. It separates in fine needles which melt at  $200^{\circ}$ – $201^{\circ}$ .

Analysis:

0.1830 gram substance gave 0.2891 gram  $\text{CO}_2$  and 0.0634 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{26}\text{H}_{28}\text{O}_4\text{Br}_4$ .	Found.
C	43.09	43.08
H	3.86	3.85

*Addition of Bromine to Methyl  $\alpha$ -Methylcinnamylidenacetate*.—When bromine is added to a solution of the methyl ester of  $\alpha$ -methylcinnamylidenacetic acid in carbon bisulphide which is kept cold in a freezing mixture, addition takes place very slowly. If a crystal of iodine be added the reaction is accelerated. The product is a tetrabromide, which separates as a solid on evaporating the solution. After recrystallizing,

first from alcohol and finally from a mixture of chloroform and alcohol, it is obtained in the form of very small colorless prisms, melting at  $128^{\circ}$ .

Analysis:

0.2593 gram substance gave 0.2882 gram  $\text{CO}_2$  and 0.0627 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{13}\text{H}_{11}\text{O}_2\text{Br}_4$	Found.
C	29.90	30.20
H	2.68	2.71

In the absence of iodine the product is a dibromide. This is formed both when the reaction mixture is cooled with ice water and kept in the dark, in which case it takes from two to three days to come to an end, and also at room temperature in the sunlight, in which case decolorization is almost instantaneous. It can be recrystallized from a mixture of ligroin and ether, from which it separates in small colorless needles melting at  $81^{\circ}$ .

Analysis:

0.1860 gram substance gave 0.2941 gram  $\text{CO}_2$  and 0.0677 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{Br}_2$	Found.
C	43.09	43.12
H	3.86	4.08

When this substance is added to an alcoholic solution of potassium iodide it readily liberates iodine in the cold, a fact which indicates that the bromine atoms are attached to adjoining carbon atoms, since in all cases hitherto investigated this result has been obtained only with substances in which they are so placed. On oxidation with potassium permanganate in acetone solution, the only product obtained was benzoic acid. When a small amount of acetic acid was added to the acetone solution before oxidation, a small amount of substance was obtained which contained halogen, but which no longer liberated iodine in alcoholic potassium iodide solution. This substance is insoluble in sodium carbonate solution. It crystallizes from ether, in which it is very readily



soluble, in clusters of fine needles melting at  $131^{\circ}$ . Its constitution has not as yet been determined, owing to the difficulty of securing sufficient material for investigation. Straus<sup>1</sup> met with similar difficulties in attempting to determine the constitution of symmetrical diphenylbutadiene by the ordinary methods of oxidation. The only satisfactory method of attack for this and similar problems is by the use of ozone as oxidizing agent, a method which was not available for the present work.

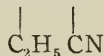
*Experiments with  $\alpha$ -Cyancinnamylidenacetic Acid,*



*Preparation.*—In preparing this acid the method followed was that of Fiquet,<sup>2</sup> heating equivalent quantities of cinnamic aldehyde and cyanacetic acid. The crude acid was recrystallized from alcohol. The yield obtained amounted to 68 per cent. of the calculated quantity.

*Ester.*—The ethyl ester was prepared both by condensation of cinnamic aldehyde with cyanacetic ester, using sodium alcoholate as a condensing agent,<sup>3</sup> and also directly from the acid by heating for a short time with a saturated solution of hydrochloric acid in alcohol.<sup>4</sup> This last method gives a quantitative yield, and may be made use of for purifying the product obtained by direct condensation, which is frequently contaminated by small quantities of the corresponding acid.

*Reactions with Magnesium Compounds:* Ethyl  $\alpha$ -Cyan- $\beta$ -ethyl- $\delta$ -phenylallylacetate,  $\text{C}_6\text{H}_5\cdot\text{CH} : \text{CH}\cdot\text{CH}\cdot\text{CH}\cdot\text{COOC}_2\text{H}_5$ .—



When solid ethyl  $\alpha$ -cyancinnamylidenacetate was added slowly to an ethereal solution of ethylmagnesium bromide, in the proportion of one molecule of ester to two and a half molecules of magnesium compound, it dissolved readily, sufficient heat being evolved to keep the ether boiling during

<sup>1</sup> Ber. d. chem. Ges., **42**, 2866.

<sup>2</sup> Ann. Chim. Phys., [6] **29**, 492.

<sup>3</sup> Bechert: J. prakt. Chem., [2] **50**, 14.

<sup>4</sup> Fiquet: *Loc. cit.*

the whole time of the reaction. The product, after decomposing with hydrochloric acid, extracting with ether, and distilling off the ether on the water bath, was a clear yellow oil which was purified by distillation under diminished pressure. The boiling point was  $220^{\circ}$  (20 mm.). A quantitative yield was obtained.

Analysis:

0.1591 gram substance gave 0.4362 gram  $\text{CO}_2$  and 0.1111 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{16}\text{H}_{19}\text{O}_2\text{N}$ .	Found.
C	74.70	74.77
H	7.39	7.79

*Hydrolysis.*—It was found possible to hydrolyze this ester in steps. For this purpose it was dissolved in absolute alcohol, and an equivalent amount of potassium hydroxide dissolved in the minimum quantity of water added. After standing in the cold for a short time, the potassium salt was precipitated with ether and purified by solution in the minimum quantity of aqueous alcohol and reprecipitation with ether. It was then thoroughly washed with ether, dried, and analyzed.

Analyses:

I. 0.1575 gram salt gave 0.0502 gram  $\text{K}_2\text{SO}_4$ .

II. 0.1706 gram salt gave 0.0547 gram  $\text{K}_2\text{SO}_4$ .

	Calculated for $\text{C}_{14}\text{H}_{14}\text{O}_2\text{NK}$ .	I.	Found.	II.
K	14.60	14.28		14.36

The acid, precipitated by hydrochloric acid from an aqueous solution of the potassium salt, separated as an oil which could not be made to crystallize. It was therefore heated on the water bath with alcoholic potassium hydroxide for two days. The alcohol was then evaporated and the residue dissolved in water and acidified. An oil separated, which solidified on standing. This was filtered off, washed with water, and recrystallized from acetone, from which it crystallizes in small prisms. A qualitative test showed the presence of nitrogen.

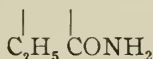
Analysis:

0.1425 gram substance gave 0.3573 gram  $\text{CO}_2$  and 0.0912 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{14}\text{H}_{17}\text{O}_3\text{N}$ .	Found.
C	68.01	68.40
H	6.88	7.19

*$\beta$ -Ethyl- $\delta$ -phenylallylmalonamic acid,*

$\text{C}_6\text{H}_5\text{.CH : CH.CH.CH.COOH}$ , melts at  $165^\circ$  and is readily



soluble in acetone, alcohol, and chloroform, slightly soluble in boiling water, and very slightly soluble in ether and ligroin.

*Oxidation.*—For this purpose 1.3 grams of the substance were dissolved in sodium carbonate and aqueous potassium permanganate added in slight excess. After filtering off the oxides of manganese and acidifying the filtrate, the products obtained were benzoic acid (0.4 gram) and a small quantity of oil which would not solidify. The formation of benzoic acid shows that the double linkage must be in the  $\gamma,\delta$  position to the amic acid group.

*$\beta$ -Ethyl- $\delta$ -phenylallylacetamide,*

$\text{C}_6\text{H}_5\text{.CH : CH.CH.CH}_2\text{.CONH}_2$ .—When  $\beta$ -ethyl- $\delta$ -phenylallyl-



malonamic acid is heated above its melting point it loses carbon dioxide and leaves  $\beta$ -ethyl- $\delta$ -phenylallylacetamide. This may be recrystallized from ether, from which it separates in fine needles melting at  $101^\circ$ .

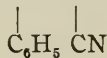
Analysis:

0.1134 gram substance gave 0.3198 gram  $\text{CO}_2$  and 0.0860 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{13}\text{H}_{17}\text{ON}$ .	Found.
C	76.84	76.93
H	8.37	8.48

*Ethyl  $\alpha$ -Cyan- $\beta,\delta$ -diphenylallylacetate,*

$\text{C}_6\text{H}_5\text{.CH : CH.CH . CH.COOC}_2\text{H}_5$ .—The reaction between  $\alpha$ -



cyanocinnamylidenacetic ester and phenylmagnesium bromide was carried out as in the corresponding experiment with ethylmagnesium bromide. In this case, however, it was necessary to keep the ethereal solution boiling on the water bath during the addition of the solid ester. The product obtained, after decomposition in the usual manner, was a yellow oil which distilled unaltered under diminished pressure. Boiling point,  $263^{\circ}$  at 18 mm.

Analysis:

0.1411 gram substance gave 0.4060 gram  $\text{CO}_2$  and 0.0830 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{20}\text{H}_{19}\text{O}_2\text{N}$ .	Found.
C	78.68	78.47
H	6.22	6.60

On oxidation with potassium permanganate the only solid product which could be obtained was benzoic acid, which was formed in the calculated quantity. The double linkage is therefore in the  $\gamma, \delta$  position to the carbethoxyl group.

*Action of Acetyl Chloride on the Magnesium Derivatives Obtained from  $\alpha$ -Cyanocinnamylidenacetic Ester.*—This reaction was carried out with both the ethylmagnesium bromide and the phenylmagnesium bromide derivatives. The solid ester was added to a solution of alkylmagnesium bromide in dry ether and heated on the water bath until reaction was complete. An ethereal solution of acetyl chloride, containing one and a half molecules of acid chloride to every atom of magnesium used, was then added slowly to the boiling solution of the magnesium derivative. A white solid separated. After boiling for from three to four hours the solid, along with the ethereal solution, was poured into iced hydrochloric acid and extracted with ether. On shaking the ethereal solution with an aqueous solution of copper sulphate a green copper salt separated in small leaflike plates. This was identified as copper cyanacetacetic ester by comparing with a specimen on hand. The filtrate left after filtering off the copper salt was distilled with steam and the residue remaining in the distilling flask extracted with ether. In the reaction with

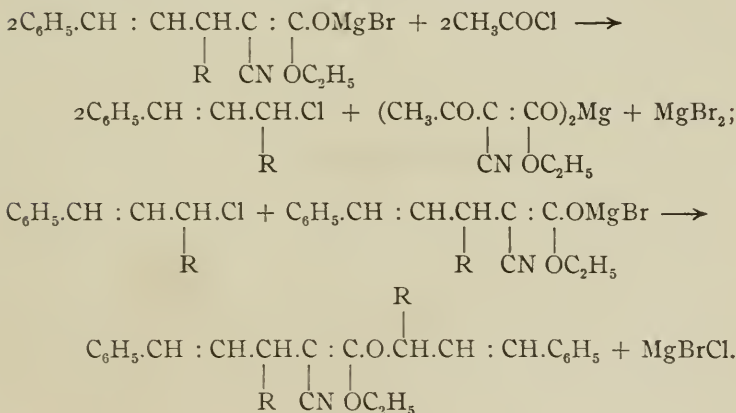
the derivative of ethylmagnesium bromide no solid product could be obtained by this treatment, but in the case of the phenylmagnesium derivative a crystalline compound separated. This was recrystallized from a mixture of chloroform and alcohol, from which it separates in the form of thick prisms. A qualitative test showed the presence of nitrogen.

Analysis:

0.1246 gram substance gave 0.3856 gram  $\text{CO}_2$  and 0.0734 gram  $\text{H}_2\text{O}$ .

	Calculated for $\text{C}_{35}\text{H}_{31}\text{O}_2\text{N}$ .	Found.
C	84.50	84.43
H	6.23	6.61

The course of the reaction is therefore as follows:



*Addition of Acid Sulphites.*—When  $\alpha$ -cyancinnamylidenacetic acid is heated for a short time with an equivalent amount of acid potassium sulphite it dissolves, giving an almost colorless solution from which hydrochloric acid precipitates no acid. This proves the existence of an acid sulphite addition product. The reaction is a reversible one, however, and the solution, when acidified with hydrochloric acid and left standing in the cold, slowly turns yellow and finally deposits a yellow precipitate of  $\alpha$ -cyancinnamylidenacetic acid. This reaction takes place more rapidly on heating, so that it was impossible to isolate the addition product.

The investigation described above was undertaken at the suggestion of Miss M. Reimer, Barnard College, to whom I wish to express my most sincere thanks. I am also greatly indebted to Dr. E. P. Kohler, Bryn Mawr College, for his kindly interest and guidance in the course of the work.

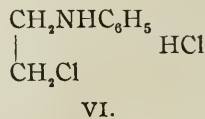
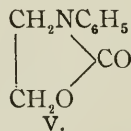
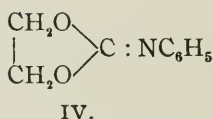
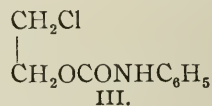
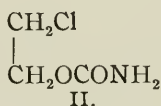
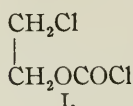
CHEMICAL LABORATORY,  
BRYN MAWR COLLEGE,  
May, 1910.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXIII.—STUDIES IN THE OXAZOLE SERIES:  
SYNTHESES OF  $\omega$ -KETOTETRAHYDROOXAZOLES.

BY TREAT B. JOHNSON AND RALPH W. LANGLEY.

In 1885, Nemirowsky<sup>1</sup> observed that phosgene and chlor-ethyl alcohol react at 200°, giving the  $\beta$ -chloroethyl ester of chloroformic acid (I). He prepared, by the action of ammonia and aniline on this chloride, the corresponding urethanes, (II) and (III), and showed that the phenyl derivative (III) is converted practically quantitatively, by treatment with alkali, into the cyclic compound, *N*-phenyl- $\omega$ -ketotetrahydro-oxazole (V). That the halogenalkyl ester of phenylcarbamic acid (III) condenses in this manner, giving a tetrahydro-oxazole derivative and not an imidocarbonate (IV), was proved by the fact that the cyclic derivative underwent hydrolysis, in the presence of hydrochloric acid, giving the hydrochloride of chloroethylaniline (VI). The prototype of this series of



cyclic compounds,  $\omega$ -ketotetrahydrooxazole, has been syn-

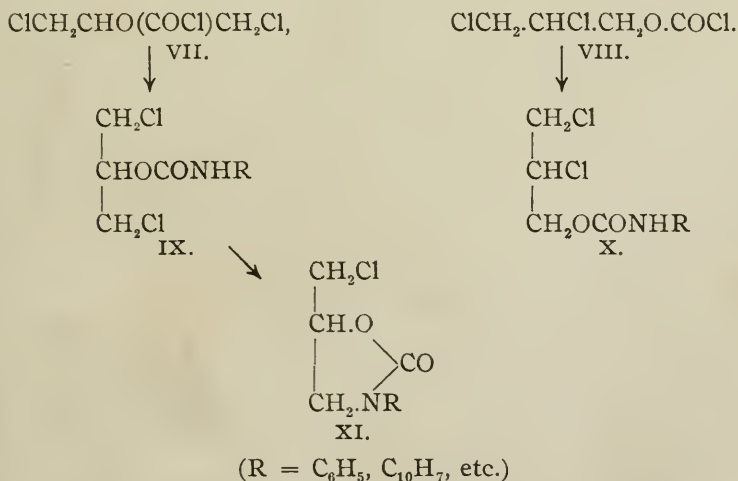
<sup>1</sup> J. prakt. Chem., [2] 31, 173.

See errata  
p. 596.



thesized by Gabriel<sup>1</sup> by the action of silver carbonate and sodium bicarbonate on the hydrobromide of bromethylamine.

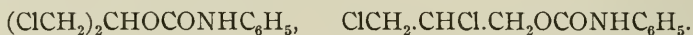
Otto<sup>2</sup> continued the study of the action of phosgene on chlorhydrins and investigated its behavior towards  $\alpha$ -monochlor- $\alpha$ -dichlor- and  $\beta$ -dichlorhydrins.  $\alpha$ -Monochlorhydrin did not react smoothly with phosgene, but from the  $\alpha$ - and  $\beta$ -dichlorhydrins acid chlorides, (VII) and (VIII), were obtained, from which he prepared a series of urethanes by the action of different amines (ammonia, aniline, naphthylamines). He also investigated the action of alkali on these compounds and showed that the urethanes (IX) obtained from  $\alpha$ -dichlorhydrin were decomposed by alkali, like the phenylurethane of chlorethyl alcohol, giving ketotetrahydrooxazoles (XI). On the other hand, all attempts to change the isomeric urethanes of  $\beta$ -dichlorhydrin (X) into cyclic compounds were unsuccessful. This interesting observation of Otto's has apparently received no attention. It was for the purpose of examining more carefully the behavior of phenylcarbamic- $\beta$ -haloid alkyl esters towards alkali that we undertook the work described in this paper.



<sup>1</sup> Ber. d. chem. Ges., **21**, 566. Gabriel and Eschenbach: *Ibid.*, **24**, 2494.

<sup>2</sup> Diss., Rostock, 1888. J. prakt. Chem., [2] **44**, 15 (1891).

Tesmer<sup>1</sup> prepared the phenylurethane of glycerol by the action of phenyl isocyanate on this alcohol, but so far as the writer is aware the phenylurethanes of the haloid esters of glycerol have not been prepared by this reaction. In fact, the only glycerol haloid esters of phenylcarbamic acid mentioned in the literature are apparently  $\beta,\beta$ -dichlorisopropyl phenylcarbamate (XII) and  $\beta,\gamma$ -dichloropropyl phenylcarbamate (XIII), described by Otto.



XII.

XIII.

We have therefore investigated the action of phenyl isocyanate on all the possible dihalohydrin derivatives of glycerol containing chlorine and bromine, *viz.*:

$\alpha$ -Dichlorhydrin,  $\text{ClCH}_2\text{CHOHCH}_2\text{Cl}$ .

$\alpha$ -Dibromhydrin,  $\text{BrCH}_2\text{CHOHCH}_2\text{Br}$ .

$\alpha$ -Chlorbromhydrin,  $\text{ClCH}_2\text{CHOHCH}_2\text{Br}$ .

$\beta$ -Dibromhydrin,  $\text{BrCH}_2\text{.CHBrCH}_2\text{OH}$ .

$\beta$ -Dichlorhydrin,  $\text{ClCH}_2\text{CHClCH}_2\text{OH}$ .

$\beta$ -Chlor- $\gamma$ -brompropyl alcohol,  $\text{BrCH}_2\text{CHClCH}_2\text{OH}$ .

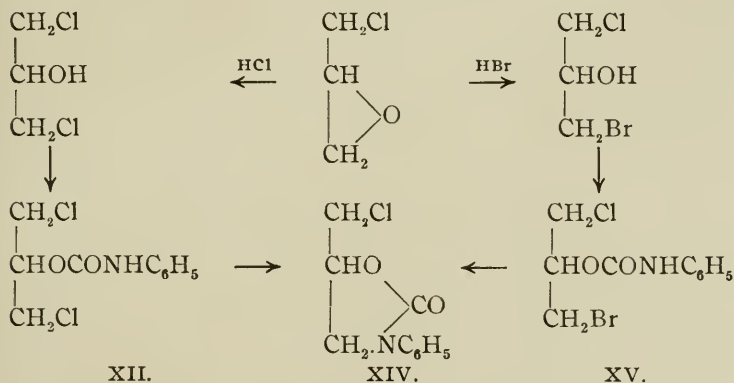
$\beta$ -Brom- $\gamma$ -chlorpropyl alcohol,  $\text{ClCH}_2\text{CHBrCH}_2\text{OH}$ .

Crystalline urethanes were obtained in every case. These compounds are characterized by their great solubility in organic solvents, the  $\beta$  derivatives being much more soluble than the  $\alpha$  forms. A remarkable feature of the series was the fact that every member, with the exception of the phenylurethanes of  $\beta$ -brom- $\gamma$ -chlorpropyl alcohol and  $\beta$ -dibromhydrin melted at  $73^\circ$ . These melted at  $75^\circ$ – $76^\circ$  and  $77^\circ$ – $79^\circ$ , respectively.

$\alpha$ -Dichlorhydrin and  $\beta$ -dichlorhydrin reacted with phenyl isocyanate, giving the same urethanes, (XII) and (XIII), as were obtained by Otto by the action of aniline on the  $\beta,\beta$ -dichlorisopropyl (VII) and  $\beta,\gamma$ -dichloropropyl (VIII) ester, respectively, of chlorformic acid. When the phenylurethane (XII) was warmed with alkali it was converted practically quantitatively into Otto's  $\beta$ -chlormethyl-N-phenyl- $\omega$ -keto-tetrahydrooxazole (XIV), melting at  $104^\circ$ . This same cyclic

<sup>1</sup> Ber. d. chem. Ges., 18, 969.

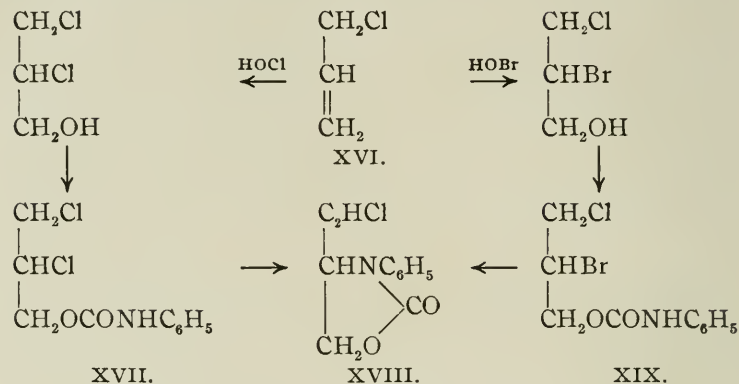
compound was also obtained when the phenylurethane of  $\alpha$ -chlorbromhydrin (XV) was treated with alkali under the same conditions. Since  $\alpha$ -dichlorhydrin and  $\alpha$ -chlorbromhydrin were prepared by addition of hydrochloric and hydrobromic acids, respectively, to epichlorhydrin, this formation of the same ketotetrahydrooxazole (XIV) from their corresponding phenylurethanes (melting at  $73^\circ$ ) is therefore new evidence that epichlorhydrin adds the two halogen acids in a similar manner, giving secondary alcohols.



While the phenylurethanes of  $\alpha$ -dihalohydrins are easily converted into ketotetrahydrooxazoles by treatment with alkali, the corresponding urethanes of the  $\beta$ -dihalohydrins show great stability under the same conditions. Otto<sup>1</sup> states that he was unable to convert the phenylurethane of  $\beta$ -dichlorhydrin (XVII) into a cyclic compound. We find that this urethane undergoes an inner condensation, in presence of alkali, giving  $\alpha$ -chlormethyl-N-phenyl- $\omega$ -ketotetrahydrooxazole (XVIII). The yield, however, was very small, since the greater proportion of the urethane underwent decomposition by the alkali. The same oxazole was also obtained when  $\beta$ -brom- $\gamma$ -chlorpropyl phenylcarbamate (XIX) was warmed with alkali. Owing to the greater reactivity of the bromine atom in this urethane (XIX), the yield of oxazole was also

<sup>1</sup> *Loc. cit.*

much better than that obtained from the corresponding dichlor compound (XVII).



$\beta$ -Chlor- $\gamma$ -bromopropyl alcohol and  $\beta$ -brom- $\gamma$ -chlorpropyl alcohol were prepared according to Henry's<sup>1</sup> method by the addition of hypobromous and hypochlorous acids to allyl chloride and allyl bromide, respectively. They boil at the same temperature and have practically the same density. The only evidence so far produced to show that they are not identical is the observation by Henry<sup>2</sup> that when oxidized they give two isomeric acids, *viz.*,  $\alpha$ -chlor- $\beta$ -bromopropionic (XX) and  $\alpha$ -brom- $\beta$ -chlorpropionic (XXI) acids:



Our observation, that the *ketotetrahydrooxazole* (XVIII), can be synthesized either from  $\beta$ -dichlorhydrin or  $\beta$ -brom- $\gamma$ -chlorpropyl alcohol, by the action of alkali on their corresponding urethanes (XVII) and (XIX), is new evidence, therefore, that the ethylene linking in allyl halides adds hypochlorous and hypobromous acids, giving primary alcohols. In other words, the halogen atoms of the acids attach themselves to that carbon atom of the ethylene group which is joined to the least number of hydrogens. The study of the oxazole compounds is being continued in this laboratory.

<sup>1</sup> Ber. d. chem. Ges., **3**, 352; **7**, 757; **8**, 2288.

<sup>2</sup> Rec. Trav. Chim., **26**, 151.

## EXPERIMENTAL PART.

*β,β'-Dichlorisopropyl Phenylcarbamate,*

CHO.CO.NH.C<sub>6</sub>H<sub>5</sub>.—This compound was prepared by warm-



ing at 100° α-dichlorhydrin with one molecular proportion of phenyl isocyanate. The reaction was complete within one hour and the urethane was obtained as a thick oil, which completely solidified on cooling. It is very soluble in ether, alcohol, chloroform and benzene, and insoluble in water. It was purified for analysis by crystallization from petroleum ether, and crystallized in burrs of fine needles melting at 73°.

Analyses:

0.1333 gram substance gave 0.1560 gram AgCl.

Nitrogen determination (Kjeldahl):

	Calculated for C <sub>10</sub> H <sub>11</sub> O <sub>2</sub> NCl <sub>2</sub> .	Found.
C	28.7	28.9
N	5.65	5.93

*β-Chlormethyl-N-phenyl-ω-ketotetrahydrooxazole,*

CH<sub>2</sub>.N.C<sub>6</sub>H<sub>5</sub> > CO.—Practically a quantitative yield of this compound was obtained as follows: Three grams of α,α-dichlorisopropyl phenylcarbamate were suspended in 20 cc. of aqueous potash (1 part alkali, 2 parts water) and heated at 100°, with shaking, for 15 minutes. Hydrochloric acid was removed by this treatment and the tetrahydrooxazole was obtained as a colorless solid insoluble in cold water. It is difficultly soluble in ligroin and ether and crystallizes from hot alcohol in slender prisms melting sharply at 104°–105° to an oil.

Nitrogen determination (Kjeldahl):

	Calculated for C <sub>10</sub> H <sub>10</sub> O <sub>2</sub> NCl.	Found.
N	6.60	6.66

*β,β'-Chlorbromisopropyl Phenylcarbamate,*

$$\text{CHO.CONHC}_6\text{H}_5\text{.—Symmetrical chlorbromisopropyl alcohol,}$$


which was prepared by addition of hydrobromic acid to epichlorhydrin, reacted at once with phenyl isocyanate, giving this carbamate. It is very soluble in alcohol and benzene and crystallizes from petroleum ether in needles melting at 73° to an oil. Analysis:

0.2223 gram substance gave 0.2546 gram AgCl + AgBr.

	Calculated for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{NClBr}$ .	Found.
Cl + Br	39.48	39.9
N	4.80	4.9

*Behavior towards Alkali.*—When the above carbamate was warmed at 100° with an aqueous solution of potassium hydroxide (1 part alkali, 2 parts water) it was converted quantitatively into *β-chlormethyl-N-phenyl-ω-ketotetrahydrooxazole*, melting at 104°. Analysis (Kjeldahl):

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_2\text{NCl}$ .	I.	Found.	II.
N	6.60	6.30		6.58

*β-Chlor-γ-brompropyl Phenylcarbamate,*

.—The *β-chlor-γ-brompropyl alcohol* which



was used for this preparation was prepared by addition of hypochlorous acid to allyl bromide. It reacted smoothly with phenyl isocyanate, when warmed on the steam bath, giving the carbamate melting at 73°. This substance is extremely soluble in alcohol and benzene and was purified by crystallization from a large volume of ligroin. Analysis:

0.2162 gram substance gave 0.2456 gram AgCl + AgBr.

	Calculated for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{NClBr}$ .	Found.
Cl + Br	39.48	39.58



A mixture of this carbamate and  $\beta,\beta'$ -chlorbromisopropyl phenylcarbamate (melting at  $73^\circ$ ) melted at  $60^\circ$ .

*$\beta$ -Brom- $\gamma$ -chlorpropyl Phenylcarbamate,*



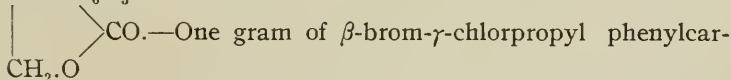
pared by the addition of hypobromous acid to allyl chloride. When this alcohol (4.0 grams) was warmed with phenyl isocyanate (2.7 grams) at  $80^\circ$  for 15 minutes, a quantitative yield of the carbamate was obtained. It was purified for analysis by recrystallization from petroleum ether and melted at  $75^\circ$ – $76^\circ$  to an oil. Analysis:

0.2169 gram substance gave 0.2494 gram  $\text{AgCl} + \text{AgBr}$ .

	Calculated for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{NClBr}$ .	Found.
Cl + Br	39.48	40.0

Mixtures of this carbamate with  $\beta,\beta'$ -chlorbromisopropyl phenylcarbamate (melting at  $70^\circ$ ) and with  $\beta$ -chlor- $\gamma$ -bromopropyl phenylcarbamate (melting at  $73^\circ$ ) melted at  $62^\circ$  and  $60^\circ$ – $69^\circ$ , respectively.

*$\alpha$ -Chlormethyl-N-phenyl- $\omega$ -ketotetrahydrooxazole,*



bamate was suspended in 20 cc. of water containing 10 grams of potassium hydroxide and the alkaline solution boiled for about 3 minutes. A heavy oil was obtained, insoluble in water, which completely solidified after washing with cold water. It was purified by recrystallization from ligroin and separated in burrs of needles melting at  $73^\circ$ – $78^\circ$  to a clear oil. A mixture of this substance and the original  $\beta$ -brom- $\gamma$ -chlorpropylphenylcarbamate melted at  $53^\circ$ – $67^\circ$ . Analysis:

	Calculated for $\text{C}_{10}\text{H}_{10}\text{O}_2\text{NCl}$ .	I.	Found.	II.
N	6.60	6.25	6.41	

This same oxazole was also obtained by digestion of  $\beta,\beta'$ -dichloropropyl phenylcarbamate with aqueous potash (1 part alkali : 2 parts water). The yield, however, was very small.

*$\beta,\beta'$ -Dibromisopropyl Phenylcarbamate,*



|  
 $\text{CHOCO}\backslash\text{NHC}_6\text{H}_5$ .—From dibromisopropyl alcohol and phenyl



isocyanate. It is very soluble in alcohol and ether, and insoluble in ligroin. It was purified by crystallization from ether and melted at  $73^\circ$ . Analyses:

0.0248 gram substance gave 0.2307 gram AgBr.

	Calculated for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{NBr}_2$ .	Found.
Br	47.47	47.94
N	4.20	4.15

*$\beta,\gamma$ -Dichloropropyl Phenylcarbamate,*



.— $\beta,\gamma$ -Dichloropropyl alcohol was prepared

by addition of hypochlorous acid to allyl chloride. It reacted smoothly with phenyl isocyanate at  $90^\circ$ , giving the above carbamate. The compound crystallizes from ligroin and melts at  $72^\circ$ – $73^\circ$  to an oil. Nitrogen determination (Kjeldahl):

	Calculated for $\text{C}_{10}\text{H}_{11}\text{O}_2\text{NCl}_2$ .	Found.
N	5.65	5.75

A mixture of this compound and  $\beta,\beta'$ -dichlorisopropyl phenylcarbamate (melting at  $73^\circ$ ) melted at  $58^\circ$ – $60^\circ$ .

*$\beta,\gamma$ -Dibromopropyl Phenylcarbamate,*



.— $\beta,\gamma$ -Dibromopropyl alcohol, which was pre-

pared according to the directions of Michael,<sup>1</sup> reacted with

<sup>1</sup> THIS JOURNAL, 2, 18.

phenyl isocyanate at  $80^{\circ}$ , giving a quantitative yield of the phenylcarbamate. It is very soluble in ether and insoluble in petroleum ether. When heated in a capillary tube it began to soften at  $72^{\circ}$  and melted to an oil at  $77^{\circ}$ – $79^{\circ}$ . A mixture of this compound and  $\beta,\beta'$ -dibromisopropyl phenylcarbamate melted at  $55^{\circ}$ – $65^{\circ}$ . Analysis:

	Calculated for $C_{10}H_{11}O_2NBr_2$ .	Found.
N	4.15	4.00

NEW HAVEN, CONN.,  
June, 1, 1910.

## BENZOPHOSPHIDE.

BY P. N. EVANS AND JENNIE TILT.

A few phosphorus compounds,  $RCOPH_2$ , analogous to the acid amides,  $RCONH_2$ , have been prepared and studied. Those described in earlier publications include only the derivatives of monochloroacetic acid,<sup>1</sup> dichloroacetic acid,<sup>2</sup> and trichloroacetic acid.<sup>3</sup>

In giving names to these compounds their analogy with acid amides has been properly emphasized by calling them acid phosphides, but it appears to the writers that this analogy is further best expressed by the names "monochloroacetophosphide," etc., rather than "monochloroacetyl phosphide," etc., as heretofore used; the name "benzophosphide," for instance, better expresses the idea that it is the acid phosphide of benzoic acid than "benzoyl phosphide," which might imply a phosphide (in the inorganic sense of a compound of phosphorus with another element or group) of the benzoyl radical. For this reason the name "benzophosphide" has been adopted.

To extend our knowledge of the acid phosphides to the aromatic compounds seemed desirable, and although its preparation has offered considerable difficulty on account of the extreme slowness of the reaction, benzophosphide,  $C_6H_5COPH_2$ , has been successfully made.

<sup>1</sup> A. Steiner: Ber. d. chem. Ges., **8**, 1178 (1875).

<sup>2</sup> P. N. Evans and C. H. Vanderkleed: THIS JOURNAL, **27**, 142 (1902).

<sup>3</sup> Cloëz: Ann. Chim. Phys., [3] **17**, 309 (1846).

*Preparation of Benzophosphide.*

*Preliminary Experiments.*—It is not necessary to give the details of the many attempts which proved either fruitless or at least very unsatisfactory; some brief notes will suffice.

Phosphine gas,  $\text{PH}_3$ , was prepared by heating together 50 grams of yellow phosphorus, 250 grams of potassium hydroxide, and 500 cc. of alcohol, and was stored in a gas holder. The gas, which consists of about equal quantities of phosphine and hydrogen and is not spontaneously inflammable, was passed into benzoyl chloride in test tubes or wash flasks, after being dried by passage through a long tube filled with lumps of dried potassium hydroxide. In some cases the gas was passed intermittently, for the sake of economy, in others the passage was continuous, and in some the apparatus was arranged to send the unabsorbed gas to a second gas holder, from which it could be passed again by merely reversing certain stopcocks.

In each experiment the liquid slowly became yellow, and then some deep yellow solid separated, probably solid hydrogen phosphide, and adhered to the glass. It was hoped and expected that the material treated with the gas would solidify as had been the case within a few hours in the preparation of dichloracetophosphide, but no such result was obtained during thirty days of contact with the gas.

The material was tested from time to time for evidences of the desired product, with positive results, as follows: The liquid was washed out with pure ether and allowed to evaporate in a desiccator containing both sulphuric acid and soda-lime, to absorb the ether and benzoyl chloride, respectively. A solid residue remained, partly insoluble in ether, the insoluble part giving qualitative tests for phosphorus with molybdate and with magnesia mixture after oxidation.

The amount of material obtained was not sufficient for satisfactory quantitative results; phosphorus estimations by the Carius method gave figures in approximate agreement with the calculated value, but also showed that an unusually long time and high temperature were necessary for complete oxidation to phosphoric acid; different analyses gave values

from 11.86 to 21.24 per cent. of phosphorus, the calculated value for the compound  $C_6H_5COPH_2$  being 22.46 per cent.

Another method of preparation tried, but without any satisfactory results, was the bringing together of benzoyl chloride and phosphonium iodide at various temperatures.

The preparation was also attempted by treating the benzoyl chloride in a test tube with pure phosphine gas under pressure, liberating it in a side-neck test tube by letting water from a dropping funnel fall upon phosphonium iodide, removing moisture and hydriodic acid from the gas by contact with potassium hydroxide, and closing the circuit by connecting the exit tube of the test tube containing the chloride with the top of the dropping funnel, introducing a mercury seal about 50 cm. deep as a safety valve. The results of these experiments were similar to those already described, and did not seem to indicate any particular advantage in this method over the less laborious one of preparing the phosphine gas from phosphorus and alcoholic potash.

*Final Preparation.*—Six wash flasks containing in all 34 grams of benzoyl chloride were connected in series, and phosphine gas, made from phosphorus and alcoholic potash, passed slowly from a gas holder through a drying tube containing solid potassium hydroxide and then through the benzoyl chloride, for six weeks, about 30 liters of gas being used. The contents of all the flasks became somewhat yellow and then crystalline.

Fifty cc. of dry ether was added to the first flask, and then enough benzoyl chloride to dissolve all the crystalline material; the liquid was transferred to the second flask, more benzoyl chloride added as required, then transferred to the third flask, and so on.

The solution of the benzophosphide in ether and benzoyl chloride so obtained was filtered, and ether slowly added, with constant stirring, as long as any precipitation resulted. The faintly yellow crystalline precipitate was filtered off and washed with ether. On drying it formed a powder and weighed 10.5 grams.

The filtrate was allowed to evaporate to about half its orig-

inal volume in a desiccator containing both sulphuric acid and solid caustic potash; considerable solid separated, which after being filtered out and washed with ether resembled the original product except in being more nearly white, and weighed 5 grams, making a total yield of 15.5 grams.

*Analysis of the Product.*

*Phosphorus.*—Determinations by the Carius method showed that long heating was necessary. The following results were obtained:

I. 0.0733 gram substance, with 20 cc. of fuming nitric acid, heated 16 hours at 200°, gave 0.0582 gram  $\text{Mg}_2\text{P}_2\text{O}_7$ .

II. 0.0843 gram substance, with 20 cc. of fuming nitric acid, heated 24 hours at 200°, gave 0.0688 gram  $\text{Mg}_2\text{P}_2\text{O}_7$ .

	Calculated for $\text{C}_6\text{H}_5\text{COPH}_2$ .	I.	Found. II.
P	22.46	22.10	22.72

*Carbon and hydrogen* were determined by combustion in a tube containing copper oxide and lead chromate. Great difficulty was experienced in effecting complete oxidation of the carbon. When heated in a porcelain boat, alone, complete burning of the charred material could not be effected in a current of oxygen. Mixed with copper oxide in the boat, and heated for 6, 10, 12, and 11 hours, respectively, in a current of oxygen, the results obtained were 53.70, 57.06, 55.64, and 59.17 per cent. of carbon, the calculated value being 60.87 per cent. In the last two cases, after heating for several hours in oxygen, the boat was withdrawn, and the contents ground with more copper oxide, the mixture replaced in the tube, and the heating in oxygen continued; in each case the potash bulbs gained in weight, but apparently the complete oxidation of the carbon had not been effected even under the extreme conditions described.

In five combustions of varying duration up to 12 hours in oxygen, the hydrogen results were as follows: 5.41, 6.05, 5.60, 6.04, and 4.59 per cent. The calculated value is 5.07 per cent.



*Properties of Benzophosphide.*

Prepared as described, it is a slightly yellowish powdery solid; in some experiments it was white. Under the microscope it appears as nearly spherical grains of fairly uniform size and strongly refractive.

On heating it shows no definite melting point, but gas bubbles begin to form and the mass to soften and contract at about  $125^{\circ}$ , continuing gradually up to  $200^{\circ}$ , and giving a rounded spongy mass. Heated in a current of dry nitrogen in a U-tube immersed in a bath, at  $75^{\circ}$  the issuing gas caused slight darkening of paper moistened with silver nitrate solution, indicating the evolution of phosphine gas, which was much more marked above  $150^{\circ}$ .

It is insoluble in water, and only slowly attacked thereby; exposed to moist air, phosphine is very slowly evolved, as indicated by the odor and the darkening action on silver nitrate paper.

It is easily soluble in absolute alcohol, but when reprecipitated by ether it is gummy and has apparently undergone some change.

It is insoluble in ether and in petroleum ether, but soluble in chloroform.

It is hoped to prepare other acid phosphides by similar reactions in this laboratory.

CHEMICAL LABORATORY,  
PURDUE UNIVERSITY, LAFAYETTE, INDIANA,  
June 4, 1910

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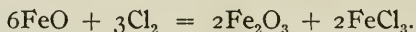
ON THE ACTION OF CHLORINE IN A SOLUTION OF  
CARBON TETRACHLORIDE AND OF CARBON  
TETRACHLORIDE ON METALLIC OX-  
IDES.

BY ARTHUR MICHAEL AND ARTHUR MURPHY, JR.

Chlorine shows the property of uniting with many of the unsaturated nonmetallic oxides to form oxychlorides, and this has been found true also for several metallic oxides; for instance, molybdenum and tungsten dioxides. On the other

hand, Weber<sup>1</sup> states that stannous oxide glows when introduced into chlorine, forming, not an addition compound, but a mixture of stannic oxide and chloride. He also heated cobalt and nickel carbonates in chlorine and obtained the corresponding chlorides, but the conditions of the experiments render it impossible to decide whether the halogen acted on undecomposed carbonates or on the oxides formed previously by the action of heat. The primary object of this investigation was to ascertain the relation between the position of metals in the periodic system and the behavior of their unsaturated oxides towards chlorine. This was done for several of the metallic groups, but as these experiments were carried out about ten years ago and there is no prospect of completing the research, we thought it advisable to publish the results we obtained.

We have used in the following experiments a solution of dry chlorine in carbon tetrachloride.<sup>2</sup> If the tetrachloride is pure and dry, such a solution will keep indefinitely and its use has many advantages. The halogen is in a state of considerable concentration, and, as has been shown in organic reactions, is, generally speaking, more reactive than in a gaseous condition; the solution may be handled easily and the percentage, or concentration, of halogen may be determined without difficulty. In all of the following experiments we have used a sufficient amount of solution to furnish the halogen in considerable excess. With ferrous oxide the reaction goes with violence, even when the chlorine solution is cooled to  $-18^{\circ}$ , ferric oxide and chloride being formed:

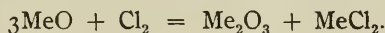


Manganous oxide also reacts energetically, but with less violence than ferrous oxide. Nickelous oxide reacts readily at room temperature, although to complete the reaction it is necessary to allow the mixture to stand some time. In order to complete the reaction with cobaltous oxide the mixture must be heated, in a sealed tube, to  $100^{\circ}$ . These three

<sup>1</sup> Jahres. d. Chem., **1861**, 147.

<sup>2</sup> Michael: J. prakt. Chem., N. F., **46**, 225.

reactions are perfectly analogous and may be represented as follows:



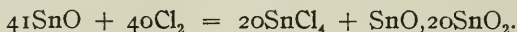
The relative facility with which these reactions proceed depends on the following relations: the affinity of the metal for chlorine, that of the monoxide for oxygen, and the energy required to separate the oxygen from the metal. On account of the greater affinity of iron than the other metals of this group for chlorine, of the easier reducibility of the monoxide of iron and its greater tendency to pass over into a more highly oxidized form than the other monoxides, it would have been safe to predict, once knowing that the reactions proceed in the above manner, that iron would show greater reactivity than manganese, cobalt and nickel monoxides. The data at hand do not permit, however, of drawing any safe conclusion in regard to the reactivity of the three last oxides among themselves, although there was a strong probability that manganese oxide would be the most reactive.

The behavior of stannous oxide is interesting. Liebig<sup>1</sup> prepared it by heating the oxalate to decomposition and obtained it as a brown substance. According to Vogel,<sup>2</sup> such a product may contain up to 4 per cent. of carbon dioxide and it is necessary to heat to redness in order to obtain a preparation completely free from dioxide. The stannous oxide thus prepared is grey. The brown stannous oxide, on addition to the chlorine solution, burns with small flashes, but the grey product reacts much more violently, the temperature rising considerably higher and the size of the flame being larger. This behavior seems anomalous, as one should expect the variety formed at the higher temperature, *i. e.*, the grey, to contain less energy and therefore to be less reactive, although it is possible that the presence of the small amount of carbon dioxide in the brown oxide may be connected, in some way difficult to understand, with the lesser reactivity. Stannic chloride is formed in each case and an insoluble, light brown oxide, which appears to be identical with the product pre-

<sup>1</sup> Ann. Chem. (Liebig), **95**, 116.

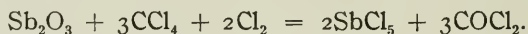
<sup>2</sup> Jahres. d. Chem., **1855**, 395.

pared by Schiff<sup>1</sup> by treating stannic acid with a solution of stannous chloride, and to which he assigned the formula  $\text{SnO}, 20\text{SnO}_2$ . In this case the reaction would be represented by the equation



Cuprous oxide is quite indifferent towards the chlorine solution, it being necessary to heat the mixture to  $250^\circ$  in order to effect a reaction. A dark brown, amorphous compound is formed, which has the composition  $\text{Cu}_2\text{OCl}_2$ . It appears, therefore, that we have here another instance of chlorine adding directly to a metallic suboxide to form an oxychloride. This cupric oxychloride,  $\text{Cu}_2\text{OCl}_2$ , has not been previously described, but a hydrated product has been obtained by the treatment of hydrated cupric chloride with calcium carbonate.<sup>2</sup>

Antimony trioxide reacts with the chlorine solution when heated to  $100^\circ$  in a sealed tube. The products of the reaction are soluble and consist of antimonious chloride and carbon oxychloride:



The reaction, therefore, proceeds with the intervention of the solvent; indeed, antimonous chloride may be the primary product, since it is formed in the action of carbon tetrachloride on antimony trioxide at  $100^\circ$ . The action of chlorine and tetrachloride may be simultaneous, however, as we have found that the action of carbon tetrachloride on some metallic oxides is materially facilitated by the presence of chlorine. We also examined the behavior of some saturated metallic oxides towards the chlorine-carbon tetrachloride solution. The action of chlorine on such oxides was investigated by R. Weber<sup>3</sup> in the research already mentioned. His method was to pass the halogen over the oxide, which was heated to the temperature of the reaction. At a high temperature—red heat or above—Weber was able to convert all the metallic

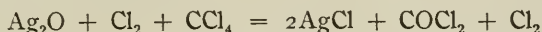
<sup>1</sup> Ann. Chem. (Liebig), **120**, 52.

<sup>2</sup> Rousseau: Compt. rend., **110**, 1261.

<sup>3</sup> Jahres. d. Chem., **1861**, 148.

oxides he examined into the corresponding chlorides; even with substances so refractory towards chlorine as magnesium and aluminium oxides.

Silver oxide reacts with the chlorine-carbon tetrachloride solution at ordinary temperature, forming silver chloride and carbonyl chloride:

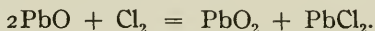


This reaction is remarkable for several reasons. Carbon tetrachloride is an exceedingly stable substance towards double decomposition and no metallic oxide is able to replace two of its halogens under the conditions of the above experiment. With silver oxide we ascertained the temperature at which it yields phosgene gas with carbon tetrachloride alone and found it required heating to the neighborhood of  $250^\circ \text{C}$ . We are, indeed, accustomed to reactions in which the combined action of two chemical forces greatly facilitates a chemical change that proceeds with difficulty with one of them alone; for instance, the comparatively easy formation of silicon chloride from silica in the presence of carbon. This, however, is easily explained, since carbon shows a marked affinity for oxygen and we have, therefore, the two chemical forces, *i. e.*, the affinity of chlorine for silicon and of carbon for oxygen, assisting each other in overcoming the chemical hindrance to the reaction, which is the energy required to separate silicon from oxygen. In the reaction between silver oxide and chlorine-carbon tetrachloride, one of the reagents, carbon tetrachloride, contains in its own molecule the conditions for a double decomposition, since the carbon possesses an affinity for the oxygen and the halogen for the silver of the oxide. It is obvious, however, from the great difference between the reaction temperatures, that the presence of free chlorine materially assists the metathesis. An explanation of this appearance of chlorine as a catalyst may be found in assuming the formation of a "polymolecule"<sup>1</sup> consisting of oxide, tetrachloride and chlorine; in such a complex the com-

<sup>1</sup> Kekulé: *Ann. Chem. (Liebig)*, **106**, 141. Michael: *Ber. d. chem. Ges.*, **34**, 4028; **39**, 2140. *THIS JOURNAL*, **39**, 3; **41**, <sup>11</sup>/<sub>2</sub>120.



bined *free chemical energy*<sup>1</sup> of the halogen atoms present would be far greater than that in the tetrachloride alone, and they should be able, therefore, to overcome the resistance involved in the separation of silver from oxygen at a lower temperature than the halogen in the tetrachloride by itself. In order to effect a reaction with lead oxide it is necessary to heat it with the chlorine solution to 100°. The tetrachloride does not enter into the reaction, which proceeds with the formation of lead peroxide and chloride:



Mercuric oxide reacts readily with gaseous chlorine, even at 0°, forming chlorine monoxide and basic chloride. The ease with which this reaction proceeds depends, however, on the preparation of the oxide; the red oxide being comparatively inert, while with a precipitated, dry product the reaction is violent. We prepared mercuric oxide in the usual manner for making chlorine monoxide, that is, by precipitating mercuric chloride with caustic soda, carefully washing the precipitate and then heating to 300°. Although this preparation reacted readily at ordinary temperature with gaseous chlorine, and gave a good yield of chlorine monoxide, it showed itself indifferent to a 10 per cent. solution of chlorine in carbon tetrachloride. In fact, a reaction took place only when the mixture was heated to 100° in a sealed tube. The products formed under these conditions were of a variable nature; mercuric chloride and a mixture of basic chlorides, which we were unable to separate, were always present. There was no decomposition of the tetrachloride in the reaction.

Finally, we investigated the behavior of some of the oxides of the metals of the sixth group towards the chlorine-carbon tetrachloride solution, and also towards carbon tetrachloride alone, since it seemed of interest to ascertain whether chlorine exerts here a catalytic influence, as in other reactions. Watts and Bell<sup>2</sup> were the first to examine the behavior of carbon tetrachloride towards metallic oxides. They heated stannic oxide in

<sup>1</sup> See J. Am. Chem. Soc., **32**, 990.

<sup>2</sup> J. Chem. Soc., **33**, 442.



a tube to redness and passed over it the tetrachloride as vapor, obtaining stannic chloride in this way. A similar experiment with tungstic acid gave a mixture of tungsten dioxydichloride,  $\text{WO}_2\text{Cl}_2$ , and oxytetrachloride,  $\text{WOCl}_4$ , while titanitic acid underwent no change. Later, Lothar Meyer,<sup>1</sup> apparently without knowledge of Watts and Bell's research, made analogous experiments, finding that the oxides of magnesium, aluminium and cerium are readily converted into chlorides, while those of boron, silicon, titanium and zirconium remain intact. Very recently, P. Camboulivès<sup>2</sup> has published an exhaustive research on this subject, having examined the conduct of a large number of oxides towards the tetrachloride in a vapor condition, and determined the temperature at which the reaction proceeds. The oxides of most of the metals from the second to the eighth group, excluding those of the platinum family, which were not examined, were found to yield the corresponding chlorides.<sup>3</sup> Our experiments<sup>4</sup> with carbon tetrachloride differ from those mentioned above in that we heated the oxides with liquid tetrachloride in sealed tubes. Chromium trioxide reacts with the chlorine-tetrachloride solution at  $150^\circ$ , yielding chromyl chloride,  $\text{CrO}_2\text{Cl}_2$ , and carbonyl chloride,  $\text{COCl}_2$ ; with the tetrachloride alone the same products are formed, but it is necessary to raise the temperature to  $170^\circ$ .

Molybdenum dioxide reacts with carbon tetrachloride at  $250^\circ$ , yielding the corresponding chloride ( $\text{MoCl}_4$ ). Molybdenum trioxide reacts with the chlorine solution at  $200^\circ$  giving a yellowish green oxychloride, mixed with unchanged trioxide; at  $225^\circ$  mixtures of yellow and green compounds, which consisted probably of molybdenum dioxydichloride and oxytetrachloride, were formed. At  $240^\circ$  the replacement of oxygen is complete and the trioxide is converted into molybdenum pentachloride. In order to effect this reaction with tetrachloride free from chlorine it is necessary to heat the mixture

<sup>1</sup> Ber. d. chem. Ges., **20**, 682.

<sup>2</sup> Compt. rend., **150**, 175.

<sup>3</sup> Niobium pentoxide and thorium dioxide yield a mixture of oxychloride and chloride; tungstic oxide gave the oxychloride.

<sup>4</sup> They were made in the winter of 1899.

to about  $280^{\circ}$ . Liechti and Kempe<sup>1</sup> prepared molybdenum tetrachloride by heating the trichloride in carbon dioxide; the pentachloride by heating the metal in chlorine. While these preparations are apparently simple the chlorides are obtained pure with difficulty, and the method just described is probably the best way to make these compounds. Camboulives obtained the pentachloride by passing carbon tetrachloride vapor over heated molybdenum trioxide, but gives a very much higher temperature, *viz.*,  $510^{\circ}$ , as the reaction temperature. We found, too, that the oxide  $\text{Mo}_3\text{O}_8$ , with liquid tetrachloride, at  $240^{\circ}$  also gives the pentachloride. By heating tungsten trioxide with the chlorine solution either tungsten oxytetrachloride or tungsten hexachloride may be prepared according to the temperature. At  $240^{\circ}$  the oxychloride ( $\text{WOCl}_4$ ) is formed; at  $280^{\circ}$  the reaction is complete and the hexachloride results. Without chlorine no action takes place at  $240^{\circ}$ , but at  $280^{\circ}$  the hexachloride is formed. These are probably the best methods to prepare the oxytetrachloride and hexachloride of tungsten. Camboulives, by his method, obtained only the oxychloride, and gives the high temperature of  $560^{\circ}$  as the temperature of reaction.

Finally, we made some experiments with the oxides of uranium. Uranium dioxide heated with carbon tetrachloride at  $250^{\circ}$ , for several hours, gives uranium tetrachloride. The oxides  $\text{UO}_3$  or  $\text{U}_3\text{O}_8$ , at the same temperature, give the pentachloride. Roscoe<sup>2</sup> first prepared the pentachloride by heating any of the oxides of uranium with carbon in a current of chlorine, but the tetrachloride is formed at the same time, which makes it difficult to obtain a pure product in this way. Camboulives obtained a mixture of tetra- and pentachlorides from uranium trioxide and gives  $360^{\circ}$  as the reaction temperature. As the pentachloride loses chlorine easily, passing over into the tetrachloride, the pentachloride is probably the primary product of the reaction and suffers partially a decomposition into the tetrachloride at the high temperature of the experiment. The method here described is undoubtedly the best way for the preparation of these chlorides.

<sup>1</sup> Ann. Chem. (Liebig), **169**, 357.

<sup>2</sup> Ber. d. chem. Ges., **7**, 1132.

This method of preparing metallic chlorides by heating the oxides with liquid carbon tetrachloride may doubtlessly be extended and, in some cases, would probably be the best manner to prepare such substances; perhaps it could be used to prepare new chlorides. There is no doubt, also, that a more careful study of the conditions of temperature will make possible in many cases a gradual replacement of oxygen by chlorine, and thus furnish a good method of preparing oxychlorides.

#### EXPERIMENTAL PART.

Carbon tetrachloride absorbs, at  $0^{\circ}$ , about 25 per cent. of its own weight of chlorine, and at ordinary temperature about 10 per cent. Such solutions will keep indefinitely in properly closed vessels, providing the tetrachloride is pure and the reagents perfectly dry. The commercial tetrachloride may be easily purified for the above purpose by treating it in the sunlight with strong hydrochloric acid and powdered potassium chlorate, in a bottle with a loosely fitting glass stopper, adding more acid and chlorate as required and shaking the bottle occasionally. It is well to keep up this treatment for a number of days. The tetrachloride is then extracted with caustic soda, finally with water, and after careful drying with phosphorus pentachloride, distilled. It is also necessary to dry the chlorine finally by passing it through a tube containing the pentoxide. In the experiments where carbonyl chloride was formed, the tubes sometimes exploded and were always under considerable pressure. We found, however, that with the use of Jena combustion tubing an explosion rarely occurred. The tetrachloride solution used in the experiments described below contained from 8 to 10 per cent. of chlorine.

#### *Ferrous Oxide.*

Ferrous oxide was prepared by heating the oxalate in a combustion tube, finally to a dull red heat, and allowing the product to cool slowly in the gases of decomposition. There was some difficulty in transferring the oxide into a vessel containing the chlorine solution without oxidation. By pass-

ing a rapid stream of dry carbon dioxide, entirely free from air, through the combustion tube, and pouring the ferrous oxide into a flask containing the chlorine solution, which was cooled to  $-15^{\circ}$ , and filled with carbon dioxide, it was possible to bring the two substances together without perceptible oxidation.

The reaction between ferrous oxide and chlorine is extremely violent; the oxide burns with a green flame, and considerable heat is evolved. The products of the reaction are ferric oxide and ferric chloride, both of which are insoluble in carbon tetrachloride. The tetrachloride was poured off and the products filtered and washed with dry carbon tetrachloride. The mixture was then dried in a vacuum to remove the tetrachloride and finally heated to constant weight at  $100^{\circ}$ . The ferric chloride was extracted with boiling water and titrated with 0.1 N silver nitrate for chlorine. The ferric oxide was weighed, dissolved in acid, reconverted into ferric oxide, and weighed again.

Weight of mixture, 1.2572 grams.

Weight of  $\text{Fe}_2\text{O}_3$ , 0.6260 gram; wt. of  $\text{Fe}_2\text{O}_3$  (reconverted), 0.6258 gram.

Weight of  $\text{FeCl}_3$ , 0.6312 gram; weight of Cl, 0.4101 gram. Calculated, 0.4100 gram.

	Calculated.	Found.
$\text{Fe}_2\text{O}_3$	49.6	49.1
$\text{FeCl}_3$	50.4	50.1

#### *Manganous Oxide.*

The manganous oxide was prepared from the oxalate, like the ferrous compound, and in introducing it into the chlorine solution the same precautions are necessary. It reacts violently, burning with a bluish flame and with the evolution of considerable heat. The products of the reaction are manganic oxide and manganous chloride, both of which are insoluble in the tetrachloride. The precipitate was treated as described above in the case of ferrous oxide; the manganous chloride was separated from the oxide by boiling with water and

the "available" oxygen in the latter determined by the iodine method.

Weight of mixture, 1.1260 grams.

Weight of  $\text{Mn}_2\text{O}_3$ , 0.6308 gram. "Available" O: Found, 0.60 gram; calculated, 0.63 gram.

Weight of  $\text{MnCl}_2$  (diff.), 0.4952 gram. Chlorine: found, 0.2855 gram; calculated, 0.2800 gram.

	Calculated.	Found.
$\text{Mn}_2\text{O}_3$	56.1	56.0
$\text{MnCl}_2$	43.9	43.7

*Nickel Monoxide.*

Nickelous oxide was prepared from dry carbonate by heating in a combustion tube until gas ceased to be given off, cooling to about  $150^\circ$ , and then passing over it a stream of dry hydrogen until the product was entirely cool. It reacted at ordinary temperatures with the chlorine solution, with a perceptible evolution of heat. The reaction is complete after standing for about an hour. The products, nickelous chloride and nickelic oxide, are insoluble in carbon tetrachloride, and were separated from the solution and prepared for analysis like the iron compounds.

Weight of mixture, 0.9632 gram.

Weight of  $\text{Ni}_2\text{O}_3$ , 0.5402 gram.

Weight of  $\text{NiCl}_2$  (diff.), 0.4280 gram. Chlorine: found, 0.2301 gram; calculated, 0.2313 gram.

	Calculated.	Found.
$\text{Ni}_2\text{O}_3$	56.0	56.3
$\text{NiCl}_2$	43.9	43.8

*Cobalt Monoxide.*

Cobaltous oxide was prepared by heating the carbonate in a combustion tube. In order to effect a reaction with the chlorine solution it is necessary to heat in a sealed tube at  $100^\circ$ , and the action is complete only after several hours. The products of the reaction are cobaltic oxide and cobaltous.



chloride, both insoluble in carbon tetrachloride. These were prepared for analysis as in the previous cases.

Weight of mixture, 0.7420 gram.

Weight of  $\text{Co}_2\text{O}_3$ , 0.4170 gram.

Weight of  $\text{CoCl}_2$  (diff.), 0.3250 gram. Chlorine: found, 0.1752 gram; calculated, 0.1767 gram.

	Calculated.	Found.
$\text{Co}_2\text{O}_3$	56.2	57.0
$\text{CoCl}_2$	43.8	42.9

#### *Stannous Oxide.*

The two varieties of stannous oxide were prepared by heating the oxalate in a combustion tube and allowing the products to cool in the gases of decomposition. The brown product, formed at a temperature just sufficient to completely decompose the oxalate, is less reactive toward chlorine than the grey variety, which is formed at a heat approaching redness. Both modifications are stable in the air, but react with chlorine solution at room temperature, giving off heat and with a flame, the reaction with the grey oxide being the more violent.

The products of the reaction are stannic chloride and a higher oxide, which has probably the composition  $\text{SnO} \cdot 20\text{SnO}_2$ . Stannic chloride is miscible with carbon tetrachloride, and cannot be completely separated from it by distillation. On fractionating, both products went over at temperatures from  $76^\circ$  to  $114^\circ$ , but at no time did either compound distil free from the other. The oxide  $\text{SnO} \cdot 20\text{SnO}_2$  is lighter in color than the oxide used in the reaction; that from brown stannous oxide being very light brown, and that from the grey oxide a light grey. When either variety was heated in the air, it added oxygen and formed stannic oxide. That the true formula of this compound is  $\text{SnO} \cdot 20\text{SnO}_2$ , is by no means certain, but it certainly is an oxide containing a little less oxygen than the stannic oxide, although the difference is too slight to establish the constitution with absolute certainty.

The oxide was separated from carbon tetrachloride and stannic chloride by decantation, washing with carbon tetra-



chloride, removing traces of the latter by warming in a vacuum, and then drying at  $100^{\circ}$  to constant weight.

1.5825 grams  $\text{SnO} \cdot 20\text{SnO}_2$  gave 1.5990 gram  $\text{SnO}_2$ .

1.1260 grams  $\text{SnO} \cdot 20\text{SnO}_2$  gave 1.1329 grams  $\text{SnO}_2$ .

The amount of the product  $\text{SnO} \cdot 20\text{SnO}_2$  obtained from the amount of stannous oxide used was very close to the calculated amount:

2.5620 gram  $\text{SnO}$  gave 1.4350 grams  $\text{SnO} \cdot 20\text{SnO}_2$ .

Calculated.

55.9

Found.

56.0

The formation of stannic chloride was shown by qualitative tests.

#### *Cuprous Oxide.*

Cuprous oxide, prepared by reducing a solution of copper sulphate with grape sugar, was dried in an air bath at  $130^{\circ}$  and then treated with the chlorine solution in a sealed tube. In order to obtain a reaction it is necessary to heat the tube to about  $250^{\circ}$ , when a dark brown amorphous compound is formed, which is the oxychloride,  $\text{Cu}_2\text{OCl}_2$ . This compound is insoluble in carbon tetrachloride and was separated and prepared for analysis as described above.

Calculated.

59.4

33.1

Found.

58.4

33.8

#### *Antimonous Oxide.*

Antimonous oxide reacts with the chlorine solution to form carbonyl chloride and antimony pentachloride. The reaction does not take place at ordinary temperatures, but readily, and in a short time, in a sealed tube at  $100^{\circ}$ . The whole of the oxide was converted into the pentachloride, which is soluble in carbon tetrachloride, but is easily separated from it by fractionation.

With carbon tetrachloride alone, antimonous oxide reacts in a tube at  $100^{\circ}$  to form antimony trichloride and carbonyl chloride, but in order to complete the reaction it has to be

heated for 24 hours. Antimony trichloride is insoluble in carbon tetrachloride and was separated and prepared for analysis as described above.

0.4210 gram  $\text{SbCl}_3$  gave 0.2629 gram  $\text{AgCl}$ .

	Calculated.	Found.
Cl	47.1	46.8

Camboulives,<sup>1</sup> by passing carbon tetrachloride vapor over the heated trioxide, also obtained the trichloride and gives  $390^\circ$  as the temperature of reaction.

#### *Silver Monoxide.*

Dry silver oxide was brought into the chlorine solution and the mixture allowed to stand for several hours, when the reaction was complete.

0.76 gram  $\text{Ag}_2\text{O}$  gave 1.084 grams  $\text{AgCl}$ , while the amount calculated is 1.086 grams.

With carbon tetrachloride alone the oxide has to be heated to about  $250^\circ$  in order to effect a reaction. The products are the same as in the presence of chlorine, *i. e.*, silver chloride and carbonyl chloride.

#### *Lead Monoxide.*

The reaction takes place at  $100^\circ$  in a sealed tube, and is complete after several hours' heating. Both the products formed, lead dioxide and lead chloride, are insoluble in tetrachloride.

1.7705 grams  $\text{PbO}$  gave 2.0517 grams of mixture; calculated, 2.0521 grams.

The chloride was separated by repeated extraction with hot water.

2.0577 grams substance gave 0.9525 gram  $\text{PbO}_2$ .

	Calculated.	Found.
$\text{PbO}_2$	46.3	46.4

#### *Mercuric Oxide.*

Mercuric oxide was prepared by precipitating the chloride with caustic potash, repeatedly extracting the precipitate

<sup>1</sup> *Loc. cit.*

with boiling water and drying at  $250^{\circ}$ . This product reacted with gaseous chlorine at room temperature and gave a good yield of chlorine monoxide. With the chlorine solution (9 per cent.) no action took place at ordinary temperature, and it was necessary to heat the mixture in a sealed tube at  $100^{\circ}$ . The tetrachloride is converted into phosgene gas, and the insoluble residue consists of a mixture of oxychlorides, varying in composition, as in different experiments they contained from 15 to 23 per cent. of chlorine ( $\text{HgCl}_2 = 26.1$  per cent. Cl).

With tetrachloride alone the oxide reacts under the same conditions, forming carbonyl chloride and basic chlorides, containing, however, less chlorine (9 to 13 per cent.).

*Chromium Trioxide.*

Chromium trioxide reacts with the chlorine solution in a sealed tube at  $150^{\circ}$ , and forms the oxychloride,  $\text{CrO}_2\text{Cl}_2$ , and carbonyl chloride. Without chlorine, the tetrachloride is somewhat less reactive, a temperature of about  $175^{\circ}$  being required. The oxychloride is soluble in tetrachloride, but may be easily separated from it by fractionation.

*Oxides of Molybdenum.*

Finely powdered molybdenum dioxide, heated in a sealed tube for several hours to  $250^{\circ}$ , gave carbonyl chloride and a brown, microscopically crystalline powder. This substance was washed with tetrachloride and dried to constant weight in a vacuum. As shown by the following chlorine estimation, it consisted of molybdenum tetrachloride.

0.4253 gram substance gave 1.0251 grams  $\text{AgCl}$ .

	Calculated.	Found.
Cl	59.7	59.6

On heating molybdenum trioxide with the chlorine solution to  $200^{\circ}$  a reaction takes place, with the formation of phosgene gas and a yellowish substance, which, however, is usually mixed with some unchanged trioxide. On heating the mixture the yellowish substance sublimes, and, to judge from this and its other properties, it is the oxychloride  $\text{MoO}_2\text{Cl}_2$ . A number of tubes were heated at temperatures

between  $200^{\circ}$  and  $225^{\circ}$  for several hours, and gave mixtures of yellow and light green compounds containing chlorine, which probably consisted of the oxychlorides  $\text{MoO}_2\text{Cl}_2$  and  $\text{MoOCl}_4$ .

By heating to  $240^{\circ}$  and maintaining this temperature for at least 3 hours, molybdenum trioxide is completely converted into pentachloride. This experiment was repeated a number of times, and we obtained each time a pure product, free from the oxychloride  $\text{MoOCl}_4$ , or any other chloride or oxychloride of molybdenum. The product melted at  $194^{\circ}$ – $195^{\circ}$ , and crystallizes from carbon tetrachloride, in which it is somewhat soluble, in fine, dark green, needlelike crystals, extremely hygroscopic, and rapidly changed by standing in air.

In order to remove the crystals from the tubes, these were opened and the crystals were washed several times with carbon tetrachloride in an atmosphere of dry carbon dioxide, drained off, and the last traces of the tetrachloride removed in a vacuum.

Molybdenum was determined in the following way: The pentachloride was dissolved in water and treated with hydrochloric acid and zinc. The compound is thus reduced to a salt of molybdenum sesquioxide, brown in color. Standard potassium permanganate was then added until the solution was colorless. Chlorine was determined by dissolving in water and precipitating with silver nitrate. The silver chloride was then filtered, dissolved in ammonia, and reprecipitated with nitric acid. The chlorine determinations are low, due perhaps to the treatment with ammonia and the subsequent precipitation. This is necessary, however, to remove any molybdenum trioxide or silver molybdate which may be formed.

1.2202 grams required 69.2 cc.  $\text{KMnO}_4$ .

0.2710 gram required 15.3 cc.  $\text{KMnO}_4$ .

0.4344 gram gave 1.1138 grams  $\text{AgCl}$ .

0.4971 gram gave 1.2861 grams  $\text{AgCl}$ .

	Calculated.	I.	Found.	II.
Mo	35.1	35.3		34.9
Cl	64.8	63.5		64.0

In order to effect a reaction between carbon tetrachloride, free from chlorine and molybdenum trioxide, it is necessary to heat somewhat higher (about  $280^{\circ}$ ) and maintain this temperature for several hours. The products are the same as when chlorine is present, carbonyl chloride and molybdenum pentachloride, and the tetrachloride solution showed the presence of free chlorine.

At temperatures ranging from  $200^{\circ}$  to  $250^{\circ}$ , molybdenum trioxide and carbon tetrachloride behave in a peculiar manner. The trioxide, without changing its crystalline structure, turns blue, the intensity of the color varying with the temperature and the length of time it is maintained. This blue product is quite stable in the air, and is neither soluble in nor decomposed by water. On boiling with nitric acid it slowly dissolves, and in every case the solution showed the presence of chlorine, the amount varying as the intensity of the blue color. Thinking that this color was perhaps due to impurities in the carbon tetrachloride, we purified a fresh lot of this substance very carefully, but found the same results as before. It is possible that the blue color is due to carbon tetrachloride combining with molybdenum trioxide, and the presence of chlorine is due to the oxidation of the tetrachloride by nitric acid. Heated to  $100^{\circ}$ , the blue color gradually disappeared; heated to  $200^{\circ}$  it disappeared rapidly and molybdenum trioxide remained. The differences in weight of the product before and after heating were very slight and determinations of the halogen varied from a mere trace to over 3 per cent., but there was no indication of a constant percentage in any two of the products.

To obtain mixed haloids of molybdenum, we made some experiments using just enough carbon tetrachloride to remove oxygen from the trioxide and a large excess of bromine, but we invariably obtained molybdenum pentachloride.

Five-tenths gram molybdenum trioxide, 2.3 grams carbon tetrachloride, and 7-10 grams of bromine were heated in a sealed tube for several hours at  $240^{\circ}$ . Dark green, rectangular crystals were formed, which showed the properties of molyb-

denum pentachloride. Qualitative tests showed no indication of bromine.

0.3194 gram substance gave 0.8365 gram AgCl.

	Calculated.	Found.
Cl	64.8	64.8

The oxide  $\text{Mo}_3\text{O}_8$ , prepared by reducing the trioxide in hydrogen, was heated in carbon tetrachloride, free from chlorine, for several hours at  $240^\circ$ . The product is molybdenum pentachloride.

#### *Oxides of Tungsten.*

Tungsten dioxide, heated for several hours in a sealed tube with carbon tetrachloride to  $250^\circ$ , is converted into tungsten tetrachloride. The substance agreed in its properties with the tetrachloride that Roscoe<sup>1</sup> obtained in the distillation of the pentachloride in carbon dioxide.

0.2018 gram substance gave 0.3501 gram AgCl.

	Calculated.	Found.
Cl	43.5	43.2

By heating tungsten trioxide in a solution of chlorine in carbon tetrachloride, either the tetraoxychloride and the hexachloride of tungsten may be obtained. Heated in a sealed tube to  $190^\circ$ – $200^\circ$  for three hours, a reaction took place, and the red, needlelike crystals of the oxychloride were formed. It melted at  $208^\circ$ .5– $210^\circ$  and was free from impurities. For analysis, the crystals were first washed with carbon tetrachloride and then, without removing them from the tube, heated to  $160^\circ$ . After some minutes, the tubes were removed from the bath and placed in a desiccator. The crystals were then dried to constant weight in a vacuum.

0.9280 gram substance gave 1.5640 grams AgCl.

	Calculated.	Found.
Cl	41.5	41.7

When tungsten trioxide is heated in the chlorine solution to  $280^\circ$ , and this temperature maintained for three to four

<sup>1</sup> Ann. Chem. (Liebig), **162**, 358.



hours, the replacement of oxygen by chlorine is complete and tungsten hexachloride results. It is possible to effect this reaction at a lower temperature, but the product is likely to contain some oxytetrachloride. In order to remove the crystals of hexachloride from the tube, and prevent decomposition, they were washed with carbon tetrachloride until free from phosgene, the tetrachloride drained off, and the tube placed in a bath and heated to  $150^{\circ}$ . The tube was then brought in a desiccator, filled with carbon dioxide, and the substance dried in a vacuum. According to Roscoe,<sup>1</sup> the hexachloride melts at  $275^{\circ}$ , but the presence of a trace of tungsten oxytetrachloride causes the melting point to be lowered to about  $100^{\circ}$ . The product we obtained melted at  $275^{\circ}$ , although it began to soften at  $271^{\circ}$ .

The analysis of the hexachloride was made by reducing the substance in hydrogen, passing the hydrochloric acid formed directly into silver nitrate solution, and weighing the silver chloride.

0.8455 gram gave 1.8230 gram AgCl.

	Calculated.	Found.
Cl	53.6	53.3

Tungsten trioxide reacts with carbon tetrachloride free from chlorine at  $280^{\circ}$ . Although a number of experiments were made at lower temperatures, we did not get the oxytetrachloride, but when the temperature was reached at which a reaction took place the hexachloride was formed at once.

The oxide  $W_3O_8$ , prepared by carefully reducing the trioxide in hydrogen, was heated with carbon tetrachloride, free from chlorine, for several hours at  $240^{\circ}$ . The tube opened under pressure with evolution of carbonyl chloride, and contained glittering black crystals. Under the microscope, two distinct varieties were noticeable; thin rectangular bundles of plates, and long, needlelike crystals, and in all probability a mixture of tungsten penta- and hexachlorides had been formed.

<sup>1</sup> Ann. Chem. (Liebig), 162, 353.

*Oxides of Uranium.*

Uranium dioxide was heated in a sealed tube with carbon tetrachloride for several hours at 250°. The reaction results in the formation of the greenish brown tetrachloride and carbonyl chloride.

0.1500 gram gave 0.2260 gram AgCl.

	Calculated.	Found.
Cl	37.2	37.2

The oxides  $\text{UO}_3$  or  $\text{U}_3\text{O}_8$ , heated in sealed tubes with the chlorine solution, or with carbon tetrachloride alone, gave in every case a mass of dark red crystals, consisting of uranium pentachloride. This compound is unstable; if heated it decomposes into the tetrachloride, the change being extremely rapid. In removing the pentachloride from the tubes, the crystals were washed with carbon tetrachloride until the washings were nearly colorless and free from carbonyl chloride, and the tube was then put in a desiccator filled with carbon dioxide and the carbon tetrachloride removed in a vacuum. When free from tetrachloride, the desiccator was again filled with carbon dioxide, and the crystals transferred from the tube to a porous plate. The compound was kept constantly in carbon dioxide.

0.4378 gram gave 0.7532 gram AgCl.

	Calculated.	Found.
Cl	42.6	42.5

## OBITUARY.

STANISLAO CANNIZZARO.

With the death of Cannizzaro there has passed away the last of that group of men who made chemistry what it was during the middle of the last century.

Cannizzaro was born at Palermo, July 13, 1826, and died May 13, 1910. Therefore, during his long lifetime chemistry grew from comparative insignificance to its present development. During his early life Cannizzaro seems to have passed a more or less erratic existence. He matriculated at the

University of Palermo in 1841 as a student of medicine, being especially interested in physiology; meeting Piria, however, he soon turned from medicine to chemistry. His chemical studies were interrupted in 1848 by the Sicilian Revolution, in which he took part as an artillery officer and a member of the Sicilian Parliament.

When the revolution was suppressed Cannizzaro escaped to Marseilles and in 1849 to Paris. Here he met Cahours, who secured him a place in Chevreul's laboratory, where he began investigations with the assistant Cloez. While in Paris Cannizzaro attended the lectures of Regnault, who was at that time carrying out his investigations on the specific heats of the elements. The influence of Regnault on Cannizzaro was very great and lasted throughout his whole career.

In 1851 the first paper by Cloez and Cannizzaro on "The Action of Cyanogen Chloride on the Amides" was published, and in this same year Cannizzaro was called to a professorship of chemistry, physics and mechanics at Alexandria in Piedmont. He remained here until 1855, when he accepted a professorship in Genoa, where he remained until 1861, and where he wrote his famous "*Sunto di un corso di filosofia chimica*," which was published in 1858. In 1861 he went to Palermo, and in 1871 to Rome, where he remained until his death.

Let us now see what Cannizzaro did that placed his name among those of the foremost men of science of his day. Eighteen years before Cannizzaro was born Dalton had proposed the atomic theory and chemists began to determine the relative weights of atoms. A difficulty arose at once. The atoms of two substances often combine in more than one proportion, and there was no method then available for determining the *number of atoms of each* that had entered into combination.

A year after the publication of Dalton's "New System of Chemical Philosophy," Gay-Lussac announced his discovery of the simple volume relations in which gases combine, and in 1811 Avogadro proposed his well-known law. He distinguished between two kinds of minute particles—the *atom* and the *molecule*—the latter being usually made up of a group of the former. The atom was thus the ultimate unit, and the molecule was made up by a combination of these atoms. Avogadro announced that in equal volumes of all gases at the same temperature and pressure there are equal numbers of molecules. When we weigh equal volumes of different gases we are weighing equal numbers of molecules of these gases. Consequently,

the weights of equal volumes of gases give their relative molecular weights.

In all such cases we must, however, choose some unit, and Avogadro took as his unit of molecular weights the *molecule of hydrogen* and referred the molecular weights of all other gases to this.

The difficulty encountered by Dalton in determining the number of atoms of any given element that enter into combination was now frequently met with by working chemists in general and especially by Berzelius. Berzelius was engaged in the study of the composition of chemical compounds and in determining atomic weights. The only way in which he could see any escape from the difficulty first met by Dalton was to lay down certain empirical rules as to the number of atoms that enter into combination with one another, but this was, of course, of no permanent value and the whole atomic theory for a time fell into disrepute.

Chemists sought to escape from the difficulty by abandoning the conception of the atom altogether and using the term "combining weight," which meant the smallest weight of an element that combines with a unit weight of a given element. The result was that they soon had a number of "combining weights" for a given element and no means of determining which was the true value. The introduction of the word "equivalents" for combining weights met the same fate, as was bound to be the case, since they were simply words introduced where a clear idea was lacking.

Theoretical chemistry was thus beset by confusion, and the chemists of this period turned their attention rather to the discovery of fact than to generalization or the building up of a science of chemistry.

Faraday discovered benzene and found that it had the same percentage composition as acetylene, and Berzelius, in 1830, introduced the term "isomerism" and applied it to compounds having the same percentage composition, but different properties. Berzelius attempted to explain the "isomerism" of compounds and the "allotropy" of the elements as due to differences in arrangement of their minute particles or atoms.

Dumas, from a study of the replacement of hydrogen by chlorine, said that one "equivalent" of chlorine replaces one "equivalent" of hydrogen and laid stress upon the so-called "type theory." He, however, failed to distinguish between equivalent, atomic weight and molecular weight and thus added to the confusion.

Liebig and Wöhler published their work on the oil of bitter almonds and showed the importance and conduct of the group "benzoyl," thus accentuating the "radical" theory, which did not solve the problem in question.

Instead of aiding the upbuilding of a science of chemistry the work from 1830 to 1860 had apparently destroyed the generalizations of the earlier period. So apparently hopeless became the situation that chemists held a congress in Carlsruhe in 1860, with the object of trying to introduce, if possible, some order into theoretical chemistry, and it was here that Cannizzaro's great work was recognized. In 1858, as already stated, he had published his "Abstract of a Course of Chemical Philosophy," and copies were handed to members of the congress.

Cannizzaro here pointed out the correctness and importance of the generalization of his countryman Avogadro, but added, "Instead of taking for your unit the weight of an entire molecule of hydrogen, take rather the half of this weight, that is to say, the quantity of hydrogen contained in a molecule of hydrochloric acid."

Cannizzaro then showed how the molecular weights of compounds can be expressed in terms of half the molecular weight of hydrogen, and laid down the following generalization: "The different weights of one and the same element contained in the various molecules are always whole multiples of one quantity, which is justly called the atom, because it invariably enters the compounds without division." \* \*

"In order to determine the atomic weight of any element, it is essential to know the molecular weights and the compositions of all or most of its compounds"—the molecular weights being, of course, determined by the use of Avogadro's law.

We can see what impression the "Abstract" made upon the congress by the following statement of Lothar Meyer: "Es fiel mir wie Schuppen von den Augen, die Zweifel schwanden, und das Gefühl ruhigster Sicherheit trat an ihre Stelle."

Cannizzaro thus recognized clearly, for the first time, the difference between molecule and atom. He showed that the apparent discrepancy between the results obtained by the law of Avogadro and that of Dulong and Petit was due to the fact that the former led to molecular weights and the latter to atomic weights, and that the two were in reality in perfect harmony with each other.

It would lead us far beyond the scope of this notice to attempt to point out even a few of the many consequences of Cannizzaro's work. He has been widely honored with mem-



bership in the various learned societies and academies of the world. He was made Senator in 1871. In 1872 he was chosen to deliver the Faraday lecture in London. He was elected an honorary member of the German Chemical Society in 1873, and in 1891 the Royal Society awarded him the Copley medal.

It was Cannizzaro who showed the chemical world the real significance of the generalization of Avogadro, and it is a noticeable coincidence that he should have been stricken down while honorary president of the Royal Academy of Sciences of Turin, which has undertaken to honor the memory of Avogadro by publishing a volume of his most important papers a century after the appearance of his epoch-making contribution to chemical science.<sup>1</sup>

Thus labored and passed away the man whom Ostwald characterizes in the lines: "In das Chaos der organischen Chemie seiner Zeit hat er begriffliche Ordnung gebracht."<sup>2</sup>

HARRY C. JONES.

## REVIEWS.

INTRODUCTION TO PHYSICAL CHEMISTRY. By HARRY C. JONES, Professor of Physical Chemistry in the Johns Hopkins University. New York: The Macmillan Co. 1910. pp. xv + 279. Price, \$1.60.

This book is an abridged edition of the larger work of the same author, "The Elements of Physical Chemistry," which is so well and favorably known that this new text scarcely needs an introduction. The plan of presentation follows very closely that of the larger book, the matter merely being shortened by judicious omissions. The result fulfils the intention of the author of giving a text much more available for undergraduate instruction. It is nonmathematical in character, an unfortunate necessity in a book of this scope, and being written in the familiar original and live style of the author, it should prove one of the most successful of the elementary texts on the subject.

JOEL H. HILDEBRAND.

AN INTRODUCTION TO PHYSICAL SCIENCE. By FREDERICK H. GETMAN, Ph.D., Associate in Chemistry, Bryn Mawr College. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. viii + 257.

The purpose of this book is unique. It is the author's belief that "the average student beginning the study of Chemis-

<sup>1</sup> For a fuller account of the work of Cannizzaro see the admirable article in "Science Progress," 5, 147. by M. M. Pattison Muir, which was used in preparing this sketch.

<sup>2</sup> Z. physik. Chem., 71, 384 (1910).



try has insufficient preparation in physical science. He can neither read his text-book intelligently nor attend a course of lectures on General Chemistry without having his attention diverted from the purely chemical side of the demonstrations by physical phenomena which he fails to understand. . . . . It is with the needs of this class of students in mind that the following pages have been written. . . . . The aim of the author has not been to compile a text-book of Physics but to bring together in logical order those physical principles which must be thoroughly understood by all who would become intelligent students of chemical science."

We are appreciating more and more, nowadays, the necessity of a thorough understanding of fundamental physical phenomena in order to gain an adequate insight into the more complex ones of chemistry. Many chemists of earlier training are lamenting a deficient knowledge of physics. By such this little book would be found instructive and entertaining reading. There is no doubt also that a review of it would be profitable for nearly every student of chemistry. In the college course, however, it is difficult to see just where it could be logically introduced. The student's course in physics should give him the training aimed at in this book. It will be interesting to hear of an instance where it has been worked into the course successfully. Whatever difficulties stand in its way for class-room work, it nevertheless deserves a hearty welcome from that large body of students who are forced to be more or less self-taught.

JOEL H. HILDEBRAND.

TECHNICAL CALCULATIONS FOR SUGAR WORKS. A Contribution to the Chemical Control of Sugar Manufacture. By OTTO MITTELSTAEDT, Technical Director of the Amstel-Suikeraffinaderij of Amsterdam. Translated from the third German edition by C. J. BOURBAKIS, Sugar Chemist. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1910. pp. xi + 117. Price, \$1.50.

This little work, the original German third edition of which appeared some eight years ago, is a clear and remarkably compact explanation of a complete scheme of calculation for the chemical control of beet-sugar factories and refineries, the scheme being based on polarization, purity and ash data.

The translator has done his work well and produced a book which will prove a useful addition to the rapidly increasing library of books on sugar technology printed in this country.

The book is specially written for the guidance of the beet-sugar chemist. Much of the subject matter dealing with refining has to do with European methods and special products which are not used here. Of course the special factors of

beet practice are not applicable in cane-sugar control. The sole worth of the book to the practical man lies in the application of the formulae to his own work, but the data which suit only special European processes and conditions may mislead him. The book will prove useful and suggestive to cane-sugar chemists as well as those in the beet-sugar industry if read with due discrimination between principles and special applications. To such its value would have been enhanced, had the calculation data been expressed in the units of measure in use here.

One naturally looks for an index in a work so handy for quick reference. Perhaps the short text (117 pages) and well-arranged table of contents make an index unnecessary.

GEORGE W. ROLFE.

LABORATORY EXERCISES IN GENERAL CHEMISTRY. By WILLIAM MARTIN BLANCHARD, Professor of Chemistry, Depauw University. Easton, Pa: The Chemical Publishing Co.

This interleaved laboratory manual contains 66 well-chosen and well-described laboratory experiments. It contains no exercises on electrolysis or on dissociation, but is on the whole an excellent collection of laboratory experiments which could be used with any text-book.

E. R.

E. MERCK'S ANNUAL REPORT OF RECENT ADVANCES IN PHARMACEUTICAL CHEMISTRY AND THERAPEUTICS. 1908. Vol. XXII. Darmstadt: E. Merck Chemical Works. 1909. pp. 394.

The Annual Reports of this firm are quite well known. They are simply a catalogue of medicinal substances and a brief statement of the published results of the past year collected from various sources. References to the literature are given. The whole collection is very useful for reference.

A. S. L.

# AMERICAN CHEMICAL JOURNAL

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[Contributions from the Chemical Laboratory of Harvard College.]

## FUROYLACETIC ESTER AND THE FURYLPIRAZO- LONES.<sup>1</sup>

[THIRD PAPER.]

BY HENRY A. TORREY AND J. E. ZANETTI.

### INTRODUCTION.

Since the discovery of acetacetic ester by Geuther in 1863,<sup>2</sup> many compounds have been prepared similar to it in general structure but having various radicals in the place of the methyl group, and as the reactions and ring formations due to the  $-\text{CO}.\text{CH}_2.\text{COOC}_2\text{H}_5$  group are exhibited by all of them to a greater or lesser degree, they have an important place in synthetic work.

Furoylacetic ester,  $\text{C}_4\text{H}_3\text{OCOCH}_2\text{COOC}_2\text{H}_5$ , prepared by Bouveault,<sup>3</sup> is of great interest to this laboratory, as it forms part of the furfurane series so long investigated by the late Professor Henry Barker Hill.

Furoylacetic ester had been but little investigated before its study was undertaken by us. But two chemists, M. M.

<sup>1</sup> The work described in this paper formed part of a thesis presented to the faculty of Arts and Sciences of Harvard University for the degree of Doctor of Philosophy by J. E. Zanetti. The experimental work was done under the direction of Professor H. A. Torrey, but as the paper was written after his death it did not have the benefit of his revision.—C. L. J.

<sup>2</sup> Jahres. d. Chem., **1863**, 323.

<sup>3</sup> Compt. rend., **125**, 1186. Bull. soc. chim., [3] **25**, 440.

Bouveault and S. S. Sandelin, had done any work upon it and this was confined to the synthesis of the ester and the preparation of three of its derivatives. Bouveault was the first to publish his work on the ester in 1899,<sup>1</sup> but did so only very briefly at the end of a communication to the Académie des Sciences on  $\alpha$ -acetylfurfurane, which he had synthesized by decomposing the ester with dilute sulphuric acid. His paper evidently escaped Sandelin's notice, for the following year that author repeated Bouveault's work step by step and published his results<sup>2</sup> without mentioning Bouveault's name. Sandelin not only prepared the furylmethyl ketone, or  $\alpha$ -acetylfurfurane, as Bouveault called it, but also the copper salt of the ester and its phenylhydrazine derivative, to which he ascribed the formula of a pyrazolone. Bouveault published a second paper<sup>3</sup> a year afterwards, calling attention to his first paper and confirming Sandelin's work without extending it. As far as we have been able to ascertain, no further work was done on furoylacetic ester until the present research was begun in the fall of 1905. Some of our earlier results we have already published.<sup>4</sup>

The objects of this research were the determination of the influence of the furyl group, both in the ester and in its pyrazolone derivatives, and the synthesis of a substance analogous to antipyrine containing the furyl group that possibly might have therapeutic value. The pyrazolone derivatives are dealt with in the second part of this paper. The first part concerns itself with the ester and its derivatives.

#### PART I. FUROYLACETIC ESTER.

The preparation of this ester, according to Sandelin's method, was described by us in our first paper,<sup>5</sup> in which we stated that our best yields were obtained by using small quantities of material, 15 grams of ethyl pyromucate and 20 grams of ethyl acetate. By using the sodium in the form of wire, however, we have found it possible to use large quantities of

<sup>1</sup> Compt. rend., *loc. cit.*

<sup>2</sup> Ber. d. chem. Ges., **33**, 492.

<sup>3</sup> Bull. soc. chim., [3] **25**, 435.

<sup>4</sup> THIS JOURNAL, **31**, 539. J. Am. Chem. Soc., **30**, 1241.

<sup>5</sup> THIS JOURNAL, **31**, 539.

material and to complete the reaction in three hours, while Bouveault<sup>1</sup> continued the reaction during 24 hours, and Sandelin<sup>2</sup> heated the mixture 7 hours after the sodium had been dissolved. Conclusive proof that the furfurane group suffers no reduction in the course of this reaction is furnished by the formation of the potassium salt of pyromucic acid from the ester by means of a concentrated solution of potassium hydroxide.

Furoylacetic ester has a slightly acid reaction and forms well-defined salts, although it does not remain dissolved in either sodic or potassic hydroxides, but this is because the potassium and sodium salts are fairly insoluble in water and separate out of the alkaline solutions when this is mixed with the ester. Dilute ammonia, however, dissolves it readily. This ester also gives a red color with ferric chloride, in alcohol solution, similar to that of acetacetic and benzoylacetic esters.<sup>3</sup>

Although Schiff<sup>4</sup> finally succeeded in preparing what appears to be the oxime of acetacetic ester by the action of hydroxylamine hydrochloride on a mixture of acetacetic ester and aniline, it is very unstable, readily splitting off a molecule of alcohol and forming methylisoxazalone, the compound that Hantzsch<sup>5</sup> obtained some years before in his study of the action of hydroxylamine on acetacetic ester. From benzoylacetic ester and hydroxylamine neither Claisen and Fedel<sup>6</sup> nor Hantzsch<sup>7</sup> succeeded in isolating the oxime, but obtained instead an isoxazalone. In the case of furoylacetic ester we found no difficulty in isolating the oxime when a mixture of sodium acetate and hydroxylamine hydrochloride was used, and, in striking contrast with the similar compound mentioned above, it is stable enough to be crystallized unchanged from weak alcohol. At the same time the isoxazalone is easily obtained by allowing the hydroxylamine to act on the

<sup>1</sup> Compt. rend., **125**, 1186.

<sup>2</sup> Ber. d. chem. Ges., **33**, 492.

<sup>3</sup> Wislicenus: *Ibid.*, **32**, 2838. Baeyer and Perkin: *Ibid.*; **16**, 2129.

<sup>4</sup> *Ibid.*, **28**, 2731.

<sup>5</sup> *Ibid.*, **24**, 497.

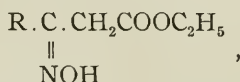
<sup>6</sup> *Ibid.*, **24**, 141.

<sup>7</sup> *Ibid.*, **24**, 502.



ester in neutral or weakly alkaline solutions or by warming the oxime with dilute alkalies.

Hantzsch<sup>1</sup> accounted for the instability of these oximes by considering them from a stereoisomeric point of view. On account of the ease of isoxazalone formation, and since neither in the case of acetacetic ester nor in that of benzoylacetic ester could isomeric oximes be isolated, he assumed that in these cases only the *syn*-oximes,



existed, the phenomenon being accounted for by considering the hydroxyl group more strongly attracted by the  $\text{—CH}_2\text{COOC}_2\text{H}_5$  group than by the R group.<sup>2</sup> The stability of the oxime of furoylacetic ester would depend, according to these considerations, on the attraction of the furyl group for the hydroxyl group being greater than that exerted by the  $\text{CH}_2\text{COOC}_2\text{H}_5$  group, or at least on a partial neutralization of the latter's influence by the furyl group in such a way that the production of the *syn*-oxime and, therefore, the formation of the isoxazalone, would be rendered more difficult than in the cases of acetacetic and benzoylacetic esters. Hantzsch<sup>3</sup> arranged various atomic groups in order of their attraction for the OH group of the oximes in the following way:

- |   |   |
|---|---|
| 1. $\text{—CH}_2\text{COOH}$                        | 6. $\text{—COC}_6\text{H}_5(o)$                                   |
| 2. $\text{—CH}_2\text{CH}_2\text{COOH}$             | 7. $\text{—C}_6\text{H}_4\text{X}(o)$                             |
| 3. $\text{—COOH}$                                   | 8. $\text{—C}_4\text{H}_3\text{S} (\text{C}_4\text{H}_3\text{O})$ |
| 4. $\text{—C}_6\text{H}_5$                          | 9. $\text{—C}_n\text{H}_{2n-1}$                                   |
| 5. $\text{—C}_6\text{H}_4\text{X}(m \text{ or } p)$ | 10. $\text{—CH}_3$  |

According to this arrangement the furyl group (8), coming after the phenyl group (4), should exert less attraction on the hydroxyl group than the former, and the oxime of furoylacetic ester should therefore be less stable than that of benzoylacetic ester. Since, as a matter of fact, the oxime of furoylacetic ester is much more stable than that of benzoyl-

<sup>1</sup> Ber. d. chem. Ges., **24**, 496.

<sup>2</sup> *Ibid.*, **24**, 1195.

<sup>3</sup> *Ibid.*, **25**, 2168.



acetic ester, the latter having never been prepared in the free<sup>1</sup> state, Hantzsch's views are inadequate to meet the situation.

Abegg<sup>2</sup> has studied the problem of the oximes from the standpoint of the dissociation theory and of electrostatics. He has shown that the stability of an oxime can be predicted from the difference in the electrostatic charges of the groups influencing the hydroxyl of the oxime. The intensity and nature of the charges can be determined from the influence of these groups on the dissociation constants of organic acids; the more negative a group the greater is the dissociation constant of the acid in which it is found. Thus he obtained the series: COOH, Cl, CH<sub>2</sub>COOH, C<sub>6</sub>H<sub>5</sub>, H, and CH<sub>3</sub>. That the CH<sub>2</sub>COOH group is more negative than either the phenyl or the methyl groups can be seen from the following constants:

(CH <sub>2</sub> COOH)COOH	(C <sub>6</sub> H <sub>5</sub> )COOH	(CH <sub>3</sub> )COOH
Malonic acid.	Benzoic acid.	Acetic acid.
K 0.158	0.0060	0.00180

The more negative the radical, therefore, in the place of R, the more stable is the resulting oxime, since the attraction of the CH<sub>2</sub>COOH group would be the more neutralized, and the less the likelihood of the isoxazolone formation. This theory of Abegg has been fully confirmed in this case. The dissociation constant of pyromucic acid is 0.707,<sup>3</sup> that is, more than ten times that of benzoic acid and nearly forty times that of acetic acid:

(C <sub>4</sub> H <sub>3</sub> O)COOH	(C <sub>6</sub> H <sub>5</sub> )COOH	(CH <sub>3</sub> )COOH
Pyromucic acid.	Benzoic acid.	Acetic acid.
K 0.0707	0.0060	0.0018

One would therefore predict from these considerations that the oxime of furoylacetic ester would be considerably more stable than that of the benzoylacetic and acetacetic esters, and this is found to be the case. That the furyl group should be less positive than the phenyl or methyl group would

<sup>1</sup> Hantzsch: *Loc. cit.*, 2169.

<sup>2</sup> Ber. d. chem. Ges., **32**, 291.

<sup>3</sup> Ostwald: Z. physik. Chem., **3**, 385.

be expected from the fact that it contains oxygen, and, although is is not as negative as the  $\text{CH}_2\text{COOH}$  group, it can at any rate partially neutralize its influence on the hydroxyl group, and make the oxime of this ester fairly stable.

The action of semicarbazide on furoylacetic ester resembles that of hydroxylamine in that the product is decidedly more stable than that from the acetacetic ester.<sup>1</sup> The latter was found by Thiele and Stangen, who investigated the action of semicarbazide on acetacetic ester, to be so unstable that even warming in alcoholic solution changed it to a pyrazolone. We found it possible, on the other hand, to crystallize the semicarbazone of furoylacetic ester from alcohol without change, obtaining a substance of constant melting point, giving on analysis values agreeing with those for the semicarbazone.

Nitrous acid reacts with furoylacetic ester giving a derivative which, in light of the work of Victor Meyer<sup>2</sup> on the action of nitrous acid on acetacetic ester, is to be considered an isonitrosofuroylacetic ester. Like the isonitroso derivatives of acetacetic ester and benzoylacetic ester, it is a white substance dissolving in alkalies with a deep orange color but insoluble in acids.

Phenyl isocyanate reacts normally with the furoylacetic ester, forming a stable addition compound similar to those of acetacetic ester and related compounds, which, as has been shown by Michael<sup>3</sup> and by Dieckmann, Hoppe and Stein,<sup>4</sup> are the addition products of phenyl isocyanate on the  $=\text{CH}_2$  group and not on the oxygen of the "enol" ( $\text{C.OH}$ ) group, as one would expect from Goldschmidt and Meissler's results.<sup>5</sup>

The resulting product may act as a *keto* and *enol* compound, but as the compound obtained from furoylacetic ester is only difficultly soluble in alkalies, the keto form must predominate and pass to the *enol* only slowly. On the other hand, the

<sup>1</sup> Ann. Chem. (Liebig), **283**, 2.

<sup>2</sup> Ber. d. chem. Ges., **10**, 2077; **11**, 320; **21**, 1293.

<sup>3</sup> *Ibid.*, **16**, 2133.

<sup>4</sup> J. prakt. Chem., [2] **60**, 317. Ber. d. chem. Ges., **38**, 22. Ann. Chem. (Liebig), **363**, 64.

<sup>5</sup> Ber. d. chem. Ges., **37**, 4627.

presence of the *enol* form is indicated by the fact that with ferric chloride a purple color is obtained as with other related substances.

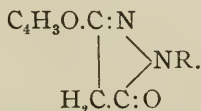
PART II. THE ACTION OF HYDRAZINES ON FUROYLACETIC ESTER.  
FURYLPYRAZOLONES.

The action of hydrazine on  $\beta$ -ketonic esters has been shown to take place in two stages. At first a hydrazone is formed by the splitting off of water and then, on heating this, alcohol is given off with the formation of a pyrazolone. In the case of acetacetic ester the hydrazone was isolated by Nef<sup>1</sup> and by Michael,<sup>2</sup> who obtained it in a pure state, while Fischer<sup>3</sup> and Knorr<sup>4</sup> had obtained it only in a very impure condition.

The first step in the reaction between the ester and the hydrazine, the separation of the water, is easily seen if no solvent is used, as the clear mixture becomes turbid on slight warming<sup>5</sup> or even on standing. The turbidity soon disappears on further warming, however, the water dissolving in the alcohol that splits off.

Although no intermediate product corresponding to the hydrazone of acetacetic ester<sup>6</sup> has been isolated in the case of furoylacetic ester, it is probable that the reaction takes place in two stages, as with phenylhydrazine. The separation of the water in the first stage causes a well-marked though transient turbidity. With hydrazine hydrate, however, this cannot be seen because of the presence of a solvent, and in the case of substituted phenylhydrazines the reaction had to be carried out at such a high temperature that the splitting off of water and alcohol were simultaneous.

When the free hydrazine or its salt, as in the case of the sodium phenylhydrazine-*p*-sulphonate, was used, a 5-pyrazolone was obtained,



<sup>1</sup> Ann. Chem. (Liebig), **266**, 71.

<sup>2</sup> THIS JOURNAL, **14**, 518.

<sup>3</sup> Ber. d. chem. Ges., **16**, 661.

<sup>4</sup> *Ibid.*, **16**, 2597.

<sup>5</sup> Knorr and Klotz: *Ibid.*, **20**, 2546.

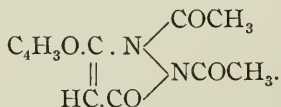
<sup>6</sup> Curtius and Jay: J. prakt. Chem., [2] **39**, 51.

Our reasons for assigning the carbonyl group to the 5-position are the facts that this reaction is entirely analogous to that of acetacetic ester, and that all our products gave a *red* isonitroso derivative which Michaelis has shown to be characteristic of 5-pyrazolones, while the 3-pyrazolones give *green* nitroso derivatives.<sup>1</sup> This point was confirmed by the preparation of 1-phenyl-5-furyl-3-pyrazolone, which gave a *green* nitroso compound with nitrous acid. In the case of the 3-furyl- and 1-phenyl-3-furylpyrazolones the action of benzaldehyde furnishes further evidence for the 5-position of the carbonyl group, since these pyrazolones react with one molecule of benzaldehyde forming red or brown compounds in which the  $C_6H_5CH=$  group is united to only one molecule of the pyrazolone, a reaction impossible in the case of 3-pyrazolones which do not contain a methylene group.<sup>2</sup>

None of these pyrazolones gives the "pyrazole blue" reaction with ferric chloride. The colors given with that reagent vary from red to green, according to the substituting groups, but do not approach the beautiful blue given by the acetacetic ester derivatives. This behavior, however, is not unknown among pyrazolones; thus the 1-methyl-3-phenyl-5-pyrazolone gives a red color with ferric chloride, but no "pyrazole blue."<sup>3</sup>

*Derivatives of 3-Furyl-5-pyrazolone.*

3-Furyl-5-pyrazolone, prepared by the action of hydrazine sulphate on furoylacetic ester, gives with acetic anhydride a monacetyl derivative in which the acetyl group is undoubtedly on the 1-nitrogen, as this contains a free imide group. The formula assigned to this product is therefore that of 1-acetyl-3-furyl-5-pyrazolone. In the case of the action of acetyl chloride in pyridine solution a diacetyl derivative is obtained and the second acetyl group is probably attached to the second nitrogen as in the formula below:



<sup>1</sup> H. Dorr: Diss., Rostock, 1906, p. 8. Michaelis: Ann. Chem. (Liebig), **350**, 288.

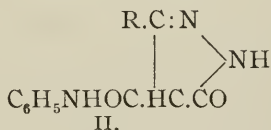
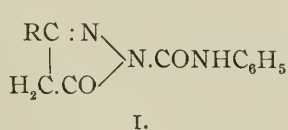
<sup>2</sup> Knorr: Ber. d. chem. Ges., **20**, 2548. Lachowicz: Monatsh. Chem., **17**, 357. Stolz: Ber. d. chem. Ges., **28**, 631.

<sup>3</sup> Michaelis and Dorn: Ann. Chem. (Liebig), **352**, 164.

It is much more likely that the pyrazolone has acted in its imine rather than in its phenol form. So far no acetyl derivatives of the latter type have been prepared, the accepted formula for these compounds having the acetyl bound to nitrogen.<sup>1</sup> That both acetyl groups are bound either to nitrogen or to nitrogen and oxygen is shown by the fact that they can be saponified with alkalis, which would not take place if one or both were bound to carbon.<sup>2</sup>

The action of phenyl isocyanate has never before been tried on the pyrazolones. Michaelis and Lampe<sup>3</sup> effected a condensation with phenylpyrazolidine, obtaining a phenyl-urea which they looked upon as a semicarbazone.

Gebhardt<sup>4</sup> has shown that phenyl isocyanate reacts on the =NH group in secondary amines and Kuhn<sup>5</sup> that the reaction takes place with amides also, as, for instance, with acetanilide. With the pyrazolone the reaction may take place in two ways. The imino group NH may be the one to react or else the CH<sub>2</sub>.C:O group may be the active one, as Michael has shown it to be the case with acetacetic ester, and similar compounds, and phenyl isocyanate. In the pyrazolones we may have "enol" and "keto" compounds, as in acetacetic ester, but it would be unlikely that the isocyanate would react with the hydroxyl group, since Michaelis<sup>6</sup> has shown that in such cases the methylene group is the active one, and moreover, Leuckardt<sup>7</sup> found that in aminophenols the isocyanate goes to the nitrogen rather than to the hydroxyl group. There are therefore two possibilities for the condensation of phenyl isocyanate with the pyrazolones:



<sup>1</sup> von Rothenburg: J. prakt. Chem., [2] **50**, 228. Curtius: *Ibid.*, [2] **50**, 511.

<sup>2</sup> Nef: Ann Chem. (Liebig), **266**, 127.

<sup>3</sup> *Ibid.*, **274**, 327.

<sup>4</sup> Ber. d. chem. Ges., **17**, 2092.

<sup>5</sup> *Ibid.*, **17**, 2883.

<sup>6</sup> Ann. Chem. (Liebig), **363**, 64.

<sup>7</sup> J. prakt. Chem., [2] **41**, 301.



Of these, formula (I) is the more probable, since phenyl isocyanate shows a great tendency to form phenylureas. Moreover, its reaction with the  $\text{CH}_2\text{CO}$  group is a slow one unless catalyzed by alkalis, so that it is doubtful if it would take place in this case at all. That the imino group is active when attached to another nitrogen in a ring compound was shown by Michaelis and Lampe in condensing the isocyanate with a pyrazolidine.

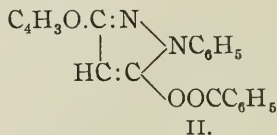
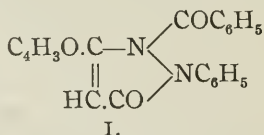
Benzaldehyde reacted with the 3-furylpyrazolone forming a light brown compound which, as analysis showed, contained only one molecule of pyrazolone condensed with one of aldehyde.

Diazobenzene chloride reacts on the  $\text{CH}_2$  group of the 3-furyl-5-pyrazolone giving a brilliant red condensation product, a reaction which is characteristic of pyrazolones in general. The resulting compound may be regarded either as a hydrazone or a diazo compound, the latter being the more generally accepted view.

*Derivatives of 1-Phenyl-3-furyl-5-pyrazolone.*

1-Phenyl-3-furyl-5-pyrazolone is a very weak base and although it forms a hydrochloride, this, if dried too long, loses its hydrochloric acid and is also readily hydrolyzed by water. Knorr obtained from the 1-phenyl-3-methylpyrazolone a similarly unstable salt, which he supposed from his analyses crystallized with one molecule of water,<sup>1</sup> although he was unable to determine the water directly. Our hydrochloride also gave low results in the chlorine determination, but as we show in the experimental part, this is due to a partial loss of hydrochloric acid during the drying.

The Schotten-Baumann reaction gives a monobenzoyl derivative with 1-phenyl-3-furyl-5-pyrazolone, and as the benzoate thus obtained is readily saponified by alkalis, there are only two possible formulas for it:



<sup>1</sup> Ann. Chem. (Liebig), **238**, 152.



In view of Knorr's<sup>1</sup> work on similar compounds from 1-phenyl-3-methylpyrazolone, formula II seems to be the more likely one.

This pyrazolone reacts with acetyl chloride, giving a monoacetyl derivative, which can be saponified by alkalies and which will therefore be considered a 1-phenyl-2-acetyl-3-furyl-5-pyrazolone.

With benzaldehyde the reaction is similar to that of the 3-furylpyrazolone, a red derivative being obtained in this case with one molecule of benzaldehyde.

With diazobenzene chloride a red 4-azobenzenepyrazolone results as in the case of the 3-furyl compound, and diazonaphthalene chloride acts in a similar way, one molecule of it condensing with one of the pyrazolone, hydrochloric acid being eliminated.

Nitrous acid acts in a normal manner on the  $\text{CH}_2$  group of the phenylfuryl-5-pyrazolone, giving, like the phenylmethylpyrazolone, an isonitroso derivative.<sup>2</sup>

*1-Phenyl-2-methyl-3-furyl-5-pyrazolone.*—Methyl iodide reacts on the 1-phenyl-3-furylpyrazolone in a manner entirely similar to the action of the same reagent on the corresponding phenylmethylpyrazolone,<sup>3</sup> adding itself to the 2-nitrogen and forming the hydriodide of the base, the pyrazolone reacting in this case as an imino compound.

By treating this salt with sodic hydroxide the free base can be obtained, which, however, is so hygroscopic and passes so easily into unmanageable tarry compounds that it has not been studied in the free state. The salts, on the contrary, crystallize very well, are decidedly stable and through them all our knowledge of this furyl analogue of "antipyrine"<sup>4</sup> has been gained. The hydrochloride, for instance, may be readily formed by passing dry hydrochloric acid into a dry ethereal solution of the base.

That the  $\text{CH}_3$  group enters in the 2-position was shown by the fact that symmetrical methylphenylhydrazine reacts on furoylacetic ester and from the reaction products it was

<sup>1</sup> Ber. d. chem. Ges., **30**, 928.

<sup>2</sup> Knorr: Ann. Chem. (Liebig), **238**, 185.

<sup>3</sup> Knorr: *Ibid.*, **238**, 203. Ber. d. chem. Ges., **17**, 2037.

<sup>4</sup> Knorr: *Ibid.*, **238**, 206.

possible to isolate the hydrochloride of 1-phenyl-2-methyl-3-furyl-5-pyrazolone identical with the one made from hydrochloric acid and the base set free from the methyl iodide addition product described above. Further evidence on this point was furnished by the decomposition of the nitroso-1-phenyl-2-methyl-3-furyl-5-pyrazolone with alkalis, symmetrical methylphenylhydrazine being obtained. From these two reactions the position of the methyl group is established; they are quite similar to those of antipyrine itself. Its salts are readily hydrolyzed by water with the formation of a brown insoluble oil, which, however, dissolves if the solution is made strongly acid. Towards ferric chloride, picric acid and platinic acid it behaves exactly like antipyrine.

Nitrous acid reacts on this body, giving a product similar to that obtained from antipyrine, which, as in the case of the 3-pyrazolones, is shown to be a true nitroso compound by its green color, but it is interesting to note that it gives a red hydrochloride which is hydrolyzed very readily to the green nitroso base. The introduction of the nitroso group in the antipyrine molecule decreases its stability and by the action of alkalis methylphenylhydrazine can be split off very easily, as mentioned above.

The pyrazolone formula has been assigned to this compound because the betain structure of the antipyrines is as yet unsettled and all the reactions of this body given here can be explained perfectly well by the original formula of Knorr.

The physiological properties of this base have not been determined as yet. The main difficulty in the way of studying them is its insolubility in water and the readiness with which its salts are hydrolyzed with the formation of an insoluble oil.

The pyrazolones included in this paper are, besides those obtained with hydrazine and phenylhydrazine, which have been studied in some detail, those made from *p*-bromophenylhydrazine, *m*-nitrophenylhydrazine and *p*-sulphonylphenylhydrazine. They are all considerably more acidic than the derivatives in which no substituting groups are present, and in their properties resemble closely the corresponding deriva-

tives from acetacetic ester except as to the "pyrazole blue" reaction. Thus the *p*-sulphonylphenylpyrazolone blackens, without melting, at 295°, in which respect it behaves like the 1-*p*-sulphonylphenyl-3-methylpyrazolone,<sup>1</sup> and like it it dissolves readily in alkalis but not in acids. The *p*-brom derivative forms white crystals, like the corresponding acetacetic ester derivative,<sup>2</sup> but melts at a lower temperature, the melting points being 160°–161° and 175°, respectively, while the 1-*m*-nitrophenyl compound resembles the acetacetic ester derivative in being colored yellow<sup>3</sup> and dissolving easily in alkalis but not in acids.

*1-Phenyl-5-furyl-3-pyrazolone*.—Following Mayer's<sup>4</sup> method for 3-pyrazolones, we attempted to obtain 1-phenyl-5-furyl-3-pyrazolone by the action of acetylphenylhydrazine and phosphorus trichloride on furoylacetic ester, but the yield did not rise above 0.1 per cent. and neither by changing the quantities of acetylphenylhydrazine nor by carrying on the reaction at varying temperatures could it be improved. Owing to scarcity of material, this work was not extended beyond the preparation of a sufficient amount of this pyrazolone for analysis and study of some of its reactions. It gave a *green* nitroso derivative with nitrous acid, while the 5-compound gave a red *isonitroso* compound, and besides this radical difference it is distinguished from its isomer by having an entirely different form of crystals, different solubilities and a slightly lower melting point. This last physical property is a remarkable one, as the 3-pyrazolones generally melt higher than the corresponding 5-compounds.<sup>5</sup>

The difficulty in preparing this pyrazolone, accepting Mayer's reaction as correct, may be due to the ester reacting mostly as a "*keto*" body, the "*enol*" compound being very slow to form. In that case the reaction would stop at the end of the first step and proceed but slowly. It may also be accounted for by the reaction of the phosphorus oxychloride on the

<sup>1</sup> Ber. d. chem. Ges., **25**, 1942.

<sup>2</sup> *Ibid.*, **33**, 2007.

<sup>3</sup> *Ibid.*, **33**, 2598.

<sup>4</sup> *Ibid.*, **36**, 717.

<sup>5</sup> Stolz: *Ibid.*, **38**, 3275.

furyl group giving resinous tarry products, as in the case of 1-phenyl-3-furyl-5-pyrazolone.<sup>1</sup>

#### EXPERIMENTAL.

*Materials Used.*—The starting material for this research was a sample of furfural which had been specially distilled for the late Professor H. B. Hill by Dr. R. Squibb, of New York. As it had stood for several years before this work was begun, it was found necessary to redistil it in order to remove polymers and decomposition products formed on standing. The fraction collected boiled between 155°–165° and constituted about two-thirds of the sample. It had a light amber color, gave the usual furfural reactions, and was not allowed to stand more than a few hours before being oxidized to pyromucic acid.

On account of the large quantities of starting material needed in this research the pyromucic acid was made by the method of Ulrich<sup>2</sup> as modified in this laboratory. This consisted in treating the furfural with a concentrated sodium hydroxide solution.

Although one-half of the furfural was lost as furfuryl alcohol which could not be recovered from the reaction products, this method had the advantage that large quantities could be handled in one operation. About two liters of furfural were treated in this manner each time, and from them 800–900 grams of fairly pure pyromucic acid, which had a light buff color and melted at 130°, were obtained.

The method of Volhard,<sup>3</sup> in which potassium permanganate is used to oxidize furfural to pyromucic acid, was tried but found too tedious for handling the large quantities needed for this work and besides did not yield directly a very pure product. The methods of Frankland and Aston<sup>4</sup> and of Freundler,<sup>5</sup> both modifications of Volhard's method, were also tried but found unsatisfactory for our purposes.

Ethyl pyromucate was obtained from this acid by dissolving it in about three to four times its weight of absolute alco-

<sup>1</sup> See Experimental Part.

<sup>2</sup> Jahres. d. Chem., **1860**, 267.

<sup>3</sup> Ann. Chem. (Liebig), **261**, 379.

<sup>4</sup> Chem. Centralb., **1901**, II, 985.

<sup>5</sup> Bull. soc. chim., **17**, 609.

hol and passing dry hydrochloric acid gas into the solution until its weight had increased by ten per cent. of that of the alcohol. The mixture was then heated in a flask attached to a reflux condenser for three or four hours, the alcohol distilled off and the residue poured into cold water, when a dark oil separated out, which, on scratching, crystallized to a mass of brown crystals. These were filtered off, dried by exposure to the air and distilled under reduced pressure, the first fraction and the residue being rejected. Thus purified, the ester consisted of long transparent prisms melting at  $34^{\circ}$ . The ethyl acetate used was obtained from Schuchardt and was thoroughly dried over calcium chloride and redistilled before using.

*Furoylacetic Ester.*—The method given by Bouveault and followed closely by Sandelin for the synthesis of furoylacetic ester consists in treating one mole of ethyl pyromucate with two moles of ethyl acetate in the presence of one atom of sodium. At the beginning of this research that method was closely followed but the poor yields obtained made it necessary to look for a more economical one. It was soon found that the best yields, 30–40 per cent. of the calculated, were obtained by using small amounts of material at a time, not more than 15 grams of ethyl pyromucate with the corresponding quantities of sodium and ethyl acetate. Whenever larger quantities than these were used, the yields were considerably lowered. The action of sodium in the form of wire was then tried and found to be much more effective and convenient, and it was also found that increasing the proportion of sodium and ethyl acetate improved the yield. With these two improvements as large a quantity of ethyl pyromucate as was available could be handled in one operation and the yield of furoylacetic ester was raised to 48 per cent. of the theoretical or to 70 per cent. of the ethyl pyromucate used.

The following proportions gave the best results: One mole of ethyl pyromucate was dissolved in 3.5 moles of ethyl acetate and into the mixture two and a half atomic weights of sodium were squeezed through a sodium press. The reaction, if the materials are thoroughly dry, begins slowly, and to start it it is generally necessary to heat on the steam bath under a



reflux condenser for about half an hour. As soon as it begins, however, it proceeds violently and the flask must be cooled by pouring water over it, else some ethyl acetate will be forced out of the top of the condenser; for this reason it is preferable to employ a copper flask and thus avoid danger of breakage on cooling. After about ten minutes the reaction becomes less violent and the solution of the sodium proceeds gently, the mixture growing dark in color. At the end of one hour a half mole of dry ethyl acetate is added to prevent the reaction mixture from caking and the heating continued for two hours longer, 3 hours in all. When all the sodium is dissolved, the reaction mixture is poured into a dish and acidified with dilute hydrochloric acid. This causes the separation of a dark brown oil which is extracted with two or three times its volume of ether and dried thoroughly over calcium chloride. The ether is then evaporated off and the residue fractionated under 20 mm. pressure. The fraction that boils below  $100^{\circ}$  consists mainly of ethyl acetate and acetacetic ester. The thermometer then rises gradually up to  $160^{\circ}$ , very little liquid distilling over, but finally when the temperature reaches  $170^{\circ}$  a light yellow oil begins to appear rapidly. The receiver is then changed and the ester, which distills over entirely within  $3^{\circ}$ , is collected. If the ethyl pyromucate has not been thoroughly purified by distillation, pyromucic acid appears at this point in the form of white needles solidifying in the condenser tube.

Furoylacetic ester thus prepared is a light yellow, heavy oil of a faint pleasant odor, miscible with alcohol and ether in all proportions but insoluble in water. When pure it is decidedly stable, darkening only on long standing. The boiling points as given by Bouveault,  $143^{\circ}$ – $145^{\circ}$  (10 mm.), and by Sandelin,  $170^{\circ}$  (20 mm.), have been verified. The ester solidifies in a mixture of solid carbon dioxide and alcohol to a mass of white crystals, and if it is allowed to cool slowly these appear as long silky needles radiating from a nucleus. With ferric chloride it gives a wine-red color and reduces ammoniacal silver oxide, depositing a mirror. The ester forms



well-defined salts, but does not remain dissolved in sodic or potassic hydroxides because the salts formed are nearly insoluble in water. In ammonia it dissolves readily.

The specific gravity was found to be 1.165 at 17°.

*The Action of Potassium Hydroxide.*—On boiling some of the ester with concentrated potassium hydroxide for some time a dark brown liquid was obtained which was acidified and extracted with ether. The extract, after thorough drying over calcium chloride, was evaporated, when dark brown needles were deposited. These were decolorized with bone black, crystallized from hot water, dried and sublimed. Thus purified they were obtained in the form of long white silky needles melting at 129°–130°, possessing the characteristic odor of pyromucic acid and giving a yellow precipitate with ferric chloride. Their solution in warm water was acid towards litmus and set free carbon dioxide from a sodium carbonate solution. These reactions show that the needles are pyromucic acid.

#### *Salts of Furoylacetic Ester.*

*Sodium Salt,  $C_9H_9O_4Na$ .*—To 4 grams of the ester dissolved in 5 cc. of alcohol were added 8 grams of sodium hydroxide dissolved in 10 cc. of water, the reaction being carried out at 0° to avoid saponification. The solution very soon became pasty from the separation of white needles of the sodium salt, which were filtered off, washed with alcohol and crystallized from hot alcohol.

Analysis:

0.2500 gram of the salt, dried over concentrated sulphuric acid *in vacuo*, gave 0.0887 gram  $Na_2SO_4$ .

	Calculated for $C_9H_9O_4Na$ .	Found.
Na	11.27	11.50

*Potassium Salt.*—When a dilute potassium hydroxide solution was used instead of sodium hydroxide, long, white, silky needles separated out, unquestionably the potassium salt, although they were not analyzed.

*Copper Salt*,  $(C_4H_5OCOCHCOOC_2H_5)_2Cu$ .—This salt was prepared according to Sandelin's directions by treating an alcohol solution of the ester with a water solution of copper acetate. The salt precipitated out of the solution in the form of small green needles, which were filtered off and dried.

Analysis:

0.5976 gram of the salt, dried *in vacuo*, gave on ignition 0.1084 gram of  $CuO$ .

	Calculated for $(C_9H_9O_4)_2Cu$ .	Found.
Cu	14.82	14.84

The copper salt crystallizes in small green needles soluble in benzene and hot alcohol but insoluble in ether. On heating it with alcohol for some time and allowing the solution to stand, thick blue plates separate out.

#### *The Action of Hydroxylamine.*

NOH

||

*Oxime of Furoylacetic Ester*,  $C_4H_5O.C.CH_2COOC_2H_5$ .—This substance was obtained by allowing one molecule of hydroxylamine hydrochloride, treated with the corresponding amount of sodium acetate, to act on one molecule of the ester, in a dilute alcoholic solution. After allowing the mixture to stand for about three hours, a mass of long white crystals separated which were filtered with suction and recrystallized from dilute alcohol. After three crystallizations the constant melting point,  $131^\circ$ – $132^\circ$ , was reached.

Analysis: The substance was dried over concentrated sulphuric acid *in vacuo*.

I. 0.2163 gram gave 0.4372 gram  $CO_2$  and 0.1058 gram  $H_2O$ .

II. 0.3995 gram of the substance gave 28.80 cc. of N at  $20^\circ$ .0 and 753 mm.

III. 0.1887 gram of the substance gave 12.6 cc. of N at  $15^\circ$ .2 and 760 mm.

IV. 0.4008 gram of the substance gave 26.70 cc. of N at  $23^\circ$  and 747 mm.

	Calculated for $C_9H_{11}O_4N$ .	I.	II. Found.	III.	IV.
C	54.82	55.13	....	....	....
H	5.58	5.48	....	....	....
N	7.11	....	8.15	7.86	7.34

Thus crystallized the oxime consists of long silky needles soluble in ether, alcohol or hot benzene, but insoluble in water or ligroin. It is soluble in alkalies and in concentrated acids.

3-Furylisoxazalone, 
$$\begin{array}{c} C_4H_3O.C:N \\ | \\ H_2C.CO \end{array} \rangle O$$
.—To 10 grams of the ester in dilute alcohol solution were added 5 grams of hydroxylamine hydrochloride and enough potassium hydroxide to make the solution strongly alkaline. The mixture was warmed for some time on the steam bath, cooled and acidified with hydrochloric acid, when a voluminous precipitate of white needles separated out. This was filtered off, washed and crystallized from dilute alcohol until it had a constant melting point.

Analysis: The substance was dried *in vacuo*.

I. 0.2194 gram gave 0.4474 gram  $CO_2$  and 0.0745 gram  $H_2O$ .

II. 0.3238 gram gave 26.55 cc. of N at 759 mm. and  $23^\circ$ .

	Calculated for $C_7H_5O_3N$ .	I.	Found.	II.
C	35.63	55.61	....	....
H	3.33	3.77	....	....
N	9.27	....	9.22	....

This isoxazalone crystallizes from dilute alcohol in long flat needles, which are colored very slightly brown if in making the compound the heating is prolonged, but if this be brief the needles can be obtained perfectly white in color. When dipped into the bath at  $145^\circ$ , the melting point of the substance is  $148^\circ$ – $149^\circ$ , but if allowed to warm with the bath, the melting point is  $147^\circ$ – $148^\circ$ . In both cases the substance decomposes on melting. This compound is soluble in water or benzene when hot, slightly so in hot ligroin, but essentially insoluble in these three solvents when cold; soluble in cold

acetone and insoluble in ether. Alkalies dissolve it readily and acids reprecipitate it unchanged. It is insoluble in concentrated hydrochloric acid.

*The Action of Semicarbazide.*

*Semicarbazone of Furoylacetic Ester*,  $C_4H_3O.C:NNHCONH_2$   
 $\begin{array}{c} | \\ CH_2COOC_2H_5 \end{array}$

This compound was formed by heating one mole of the ester, in dilute alcohol solution, with one mole of semicarbazide hydrochloride and the corresponding amount of sodium acetate. After standing for a few hours white crystals separated out. These were filtered off, washed with water and recrystallized from absolute alcohol until the melting point became constant.

Analysis: The substance was dried *in vacuo*.

I. 0.1953 gram gave 30.95 cc. of N at 27°.5 and 757 mm.

II. 0.2502 gram gave 41.38 cc. of N at 22°.5 and 747 mm.

	Calculated for $C_{10}H_{13}O_4N_3$ .	I.	Found.	II.
N	17.57	17.55		18.37

The semicarbazone crystallizes in small, flat, rhombic plates which decompose slightly on melting. They are soluble in hot absolute alcohol, hot benzene and hot chloroform, but insoluble in hot or cold ligroin.

*The Action of Nitrous Acid.*

*Isonitrosyfuroylacetic Ester*,  $C_4H_3OCOC(:NOH)COOC_2H_5$ .—To 5 grams of furoylacetic ester in dilute acetic acid were added slowly 4 grams of sodium nitrite. On allowing the solution to stand for about two hours an abundant white, flocculent precipitate separated out. This was filtered off and crystallized from hot water, whence it was obtained in the form of small white needles having the constant melting point 128°–129°.

Analysis: The substance was dried *in vacuo*.

I. 0.2317 gram gave 0.4394 gram  $CO_2$  and 0.0955 gram  $H_2O$ .

II. 0.3035 gram gave 18.62 cc. of N at 25°.1 and 773 mm.

	Calculated for $C_9H_9O_5N$ .	I.	Found.	II.
C	51.19	51.72	....	....
H	4.26	4.59	....	....
N	6.63	....	....	6.96

The isonitrosofuroylacetic ester is soluble in alcohol, ether, benzene, and hot water. Alkalies dissolve it readily, giving an orange solution from which the white nitroso derivative is reprecipitated on acidifying.

*The Action of Phenyl Isocyanate.*

Anilide of Furoylmalonic Ester,  $C_4H_3OCOCHCONHC_6H_5$ .—



To 7.7 grams of the ester were added 5 grams of phenyl isocyanate in 5 cc. of benzene and a small amount of the sodium salt of the ester to catalyze the reaction. The mixture quickly thickened to a viscous oil which, on the addition of ether, gave a precipitate of white needles. These, when filtered off and crystallized from acetic acid, melted at 143°. Two crystallizations from 80 per cent. alcohol raised the melting point to 144°–146°.

Analysis: The substance was dried *in vacuo*.

I. 0.2197 gram gave 0.5092 gram  $CO_2$  and 0.1027 gram  $H_2O$ .

II. 0.2940 gram gave 13.25 cc. of N at 20°.2 and 760 mm.

	Calculated for $C_{16}H_{15}O_5N$ .	I.	Found.	II.
C	63.79	63.22	....	....
H	5.00	5.24	....	....
N	4.65	....	....	5.13

This compound crystallizes in perfectly white needles, soluble in hot glacial acetic, hot alcohol or hot water, but essentially insoluble in all the above solvents when cold; insoluble in ether; in benzene or ethyl acetate it dissolves slightly in the cold, readily on warming. In alkalies it dissolves with difficulty in the cold; with ferric chloride in alcohol solution a purple color is obtained. If in taking the melting

point, the substance is allowed to warm up with the bath it begins to soften at about  $138^{\circ}$  and melts completely at  $146^{\circ}$ . When dipped in the bath at  $143^{\circ}$  and warmed up slowly the melting point is  $148^{\circ}$ – $150^{\circ}$ , but it does not melt at  $144^{\circ}$  when held at that temperature for some time.

3-Furylpyrazolone,  $C_4H_3O.C:N$   

$$\begin{array}{c} | \\ H_2C.C > NH. \\ || \\ O \end{array}$$
—This compound was

made by heating a dilute alcohol solution of furoylacetic ester with hydrazine sulphate and sodium acetate in molecular proportions. It can also be obtained by heating the ester with a solution of hydrazine hydrate, neutralizing with acetic acid and salting out with sodium acetate. The pyrazolone separates out as a brown crystalline powder, which can be obtained perfectly white by washing with ether and crystallizing from dilute methyl alcohol.

Analysis: The substance was dried *in vacuo*.

I. 0.2073 gram of the substance gave 0.4290 gram  $CO_2$  and 0.0813 gram  $H_2O$ .

II. 0.1652 gram of the substance gave 27.22 cc. of N at  $22^{\circ}.4$  and 756 mm.

	Calculated for $C_7H_5O_2N_2$ .	I.	Found.	II.
C	56.00	56.44	.	....
H	4.00	4.41	.	....
N	18.66	....	.	18.47

The pyrazolone crystallizes in small rectangular plates which begin to decompose at about  $200^{\circ}$ , finally blackening completely and melting at  $223^{\circ}$ . It is soluble in methyl or ethyl alcohol or warm glacial acetic acid, and slightly soluble in water or ether. Alkalies and acids dissolve it readily. In an alcoholic solution diluted with water it reacts acid towards litmus. With nitrous acid (sodium nitrite and hydrochloric acid) it gives a deep red solution from which no precipitate can be obtained either by neutralizing or making alkaline. It gives precipitates with chlorauric or chloroplatinic acids and a white flocculent precipitate with silver nitrate. It does not give the "pyrazole blue" reaction.



*Picrate*,  $C_7H_6N_2O_2 \cdot C_6H_5(NO_2)_3OH$ .—The picrate was obtained as a light yellow precipitate by adding an alcoholic solution of the pyrazolone to a saturated aqueous solution of picric acid. The precipitate was filtered off and crystallized from a mixture of alcohol and benzene.

Analysis: The substance was dried *in vacuo*.

0.1191 gram gave 19.72 cc. of N at  $21^\circ$  and 767 mm.

	Calculated for $C_{13}H_9O_9N_5$ .	Found.
N	18.47	18.98

The picrate crystallizes in small prisms with rounded ends, decomposing completely at  $192^\circ$ , although the change begins considerably below  $190^\circ$ . It is soluble in alcohol, slightly soluble in hot benzene, or hot water, but insoluble in ether.

*1-Acetyl-3-furyl-5-pyrazolone*,  $C_4H_3O.C : N$   
 $\begin{array}{c} | \\ H_2C.CO \end{array} \rangle N.COCH_3$ .—On

warming the pyrazolone with a slight excess of acetic anhydride and pouring the reaction product into cold water, an oil separates out which, after a while, crystallizes to a mass of small radiating needles. These were filtered off, dried, and crystallized until they showed a constant melting point.

Analysis:

0.1522 gram of the substance dried *in vacuo* gave 20.61 cc. N at  $27^\circ$  and 759 mm.

	Calculated for $C_9H_5O_3N_2$ .	Found.
N	14.59	14.93

This substance crystallizes in long white needles melting at  $153^\circ$ – $154^\circ$  to a viscous liquid. It is soluble in alcohol, hot benzene or hot ligroin, but insoluble in ether or in water.

On boiling with dilute sodium hydroxide to complete solution the acetyl group is split off and on neutralizing with acetic acid the pyrazolone is obtained as a precipitate of minute rectangular plates melting at  $220^\circ$ .

*1,2-Diacetyl-3-furyl-5-pyrazolone*,  $C_4H_3O.C.N$   
 $\begin{array}{c} \parallel \\ HC.CO \end{array} \rangle N.COCH_3$ .—

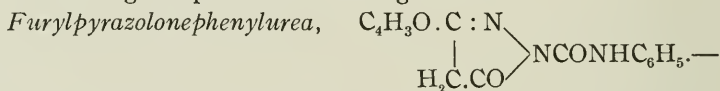
This compound was obtained by adding acetyl chloride to a pyridine solution of the pyrazolone and pouring the reaction mixture into cold water. The oil that separated out soon solidified and the dried product was crystallized from ligroin until its melting point was constant.

Analysis:

0.1689 gram of the substance, dried *in vacuo*, gave 18.78 cc. N at 26°.5 and 757 mm.

	Calculated for $C_{11}H_{10}O_4N_2$ .	Found.
N	11.96	12.26

This diacetyl derivative crystallizes in long white silky needles melting at 102° and soluble in ether, alcohol or benzene, but insoluble in water. On boiling with dilute sodium hydroxide to complete solution both acetyl groups are saponified and 3-furyl-5-pyrazolone is obtained, crystallizing in small rectangular plates and melting at 220°.



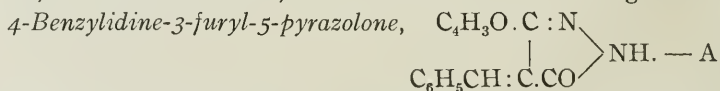
This compound was prepared by the action of phenyl isocyanate on the pyrazolone suspended in benzene. After washing off the excess of phenyl isocyanate, it was crystallized from 90 per cent. alcohol until the melting point became constant.

Analysis:

0.1350 gram of the substance, dried *in vacuo*, gave 18.65 cc. N at 27° and 765 mm.

	Calculated for $C_{14}H_{11}O_3N_3$ .	Found.
N	15.62	15.33

This compound melts at 192° and is soluble in hot chloroform, alcohol or benzene, but insoluble in water or ligroin.



glacial acetic acid solution of the pyrazolone was heated with an excess of benzaldehyde for about fifteen minutes on the steam bath. The solution thickened with the separation of a

brown precipitate which, after thorough washing, yielded a light brown powder. As this could not be crystallized, it was repeatedly washed with ether and alcohol to remove any unconverted pyrazolone and benzaldehyde, dried and analyzed.

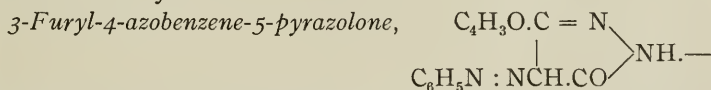
Analysis:

0.2081 gram of the substance dried *in vacuo* gave 20.52 cc. N at 18°.5 and 766 mm. pressure.

	Calculated for $C_{14}H_{10}O_2N_2$ .	Found.
N	11.75	11.47

This compound is insoluble in most organic solvents. When heated with nitrobenzene or acetophenone, some goes into solution, but on cooling only a very small amount separates out. It does not melt at 300°. Heated with sodium hydroxide solution, it gives off an odor of benzaldehyde. Concentrated sulphuric acid dissolves it, giving a red solution.

On heating the pyrazolone in a similar manner with salicylic aldehyde instead of benzaldehyde a substance was obtained, infusible at 260°, soluble in ligroin, alcohol, alkalies and acids, but insoluble in ether or in water. This is probably an analogous condensation product with salicylic aldehyde, but it was not analyzed.



To 2 grams of the pyrazolone in sodium hydroxide solution were added 0.8 gram of aniline carefully diazotized with the required amount of sodium nitrite and hydrochloric acid. A red precipitate separated at once which was filtered off and crystallized from alcohol until it had a constant melting point.

Analysis:

0.1197 gram of the substance dried *in vacuo* gave 24.10 cc. N at 25°.6 and 752 mm.

	Calculated for $C_{13}H_{10}O_2N_4$ .	Found.
N	22.05	22.15

This azo derivative crystallizes from alcohol in beautiful

red, transparent prisms, melting at  $182^{\circ}$ – $183^{\circ}$  to a thick viscous liquid adhering to the sides of the melting-point tube. It is slightly soluble in alcohol, ether or benzene, in the cold, and readily in the warm solvent.

*1-Phenyl-3-furyl-5-pyrazolone*,  $C_4H_5OC:N$   
 $\begin{array}{c} | \\ H_2C.CO \end{array} \rangle NC_6H_5$ . — This

compound was prepared by allowing one molecule of phenylhydrazine to react on one molecule of furoylacetic ester at the temperature of the steam bath, according to the method of Sandelin.<sup>1</sup> Very soon after the warming is begun the mixture becomes turbid, probably from the separation of water; this turbidity disappears rapidly, however, and after 10 or 15 minutes' heating the mass solidifies from the separation of pyrazolone, which can be obtained pure by washing with ether and crystallizing from hot absolute alcohol. Thus purified, the pyrazolone consists of small leaflets appearing under the microscope as minute rhombic plates. The melting point as given by Sandelin,  $179^{\circ}$ , was found to be correct. *1-Phenyl-3-furyl-5-pyrazolone* is readily soluble in alkalies or strong acids. With ammonia, on standing, it gives a purplish red solution and with chlorplatinic or chlorauric acid, brown precipitates. It does not combine with picric acid, neither does it give the "pyrazole blue" reaction. If boiled with ferric chloride in alcohol solution a deep red color is obtained, and on pouring this into water a gray precipitate separates which dissolves in chloroform with a deep red color. Aqueous ferric chloride solution, even when concentrated, is without action on this pyrazolone.

*Hydrochloride*,  $C_{13}H_{10}O_2N_2HCl$ .—Into a suspension of the pyrazolone in absolute alcohol dry hydrochloric acid gas was passed until all the pyrazolone was dissolved. The solution was then poured into a large excess of ether which caused the separation of a colorless oil, solidifying on scratching to a mass of white crystals. These were filtered off, thoroughly washed with ether and crystallized from a mixture of alcohol and ethyl acetate or of alcohol and benzene. The per-

<sup>1</sup> Ber. d. chem. Ges., **33**, 492.

fectly white crystals were dried over concentrated sulphuric acid, then over caustic potash. Unless the drying was brief, decomposition quickly set in, the color changing to brown. In the first two analyses the drying was carried on *in vacuo* for a long time, in the third it lasted only four hours and the air was not exhausted.

Analysis:

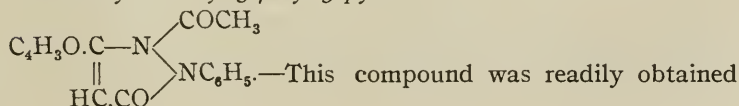
- I. 0.2441 gram gave 0.1213 gram AgCl.  
 II. 0.2443 gram gave 0.1198 gram AgCl.  
 III. 0.2840 gram gave 0.1440 gram AgCl.

	Calculated for $C_{13}H_{11}O_2N_2Cl$ .	I.	Found. II.	III.
Cl	13.52	12.29	12.12	12.54

The hydrochloride crystallizes in small white needles, soluble in alcohol or hot ethyl acetate, but insoluble in ether, benzene, or ligroin. Water hydrolyzes it, forming the pyrazolone. It is soluble in concentrated hydrochloric acid and melts at  $122^{\circ}$ – $123^{\circ}$  with decomposition.

Although the results of these analyses are a per cent. or more below the calculated values they leave no doubt as to the composition of the substance. The low percentage of chlorine was probably due to a loss of hydrochloric acid during the drying, for, as was already stated, there was a visible decomposition unless the drying was very brief, and the longer the drying the less was the amount of chlorine obtained. The only other probable hypothesis is that the salt contained half a molecule of alcohol, which would give 12.40 per cent. for chlorine, but in this case the specimen dried for 4 hours would have contained less chlorine than those dried for a longer time, whereas in fact just the reverse was the case. We feel, therefore, that this second hypothesis should be rejected, even although Knorr, from chlorine determinations only, thought the hydrochloride of his 1-phenyl-3-methylpyrazolone contained one molecule of water.

*1-Phenyl-2-acetyl-3-furyl-5-pyrazolone*



by dissolving the pyrazolone in boiling acetic anhydride and pouring the solution into water, when an oil separated out, which, on scratching, crystallized to a yellowish white mass. This was filtered off and recrystallized from ligroin until it had a constant melting point.

Analysis:

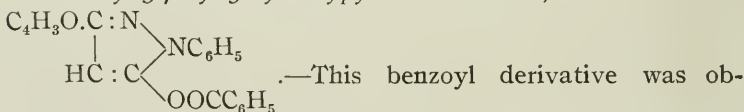
0.4196 gram of the substance dried *in vacuo* gave 39.81 cc. N at 25° and 756 mm.

	Calculated for $C_{15}H_{12}O_3N_2$ .	Found.
N	10.44	10.52 .

The melting point of this compound is not very sharp, lying between 69°–72°. Under the microscope the crystals appear as flat, transparent prisms, slightly yellow in color. They are soluble in alcohol or benzene without difficulty, but insoluble in cold ligroin.

By boiling with alcoholic potash the acetyl group is split off and on acidifying with acetic acid the pyrazolone is precipitated out in the form of flat rhombic plates melting at 178°.

*1-Phenyl-3-furyl-5-hydroxypyrazole Benzoate*,



tained by the Schotten-Baumann reaction, by dissolving the pyrazolone in sodium hydroxide and adding an excess of benzoyl chloride. After some time a yellowish mass of crystals separated out, which were finally filtered off, washed and crystallized until the melting point was constant.

Analysis:

0.2084 gram of the substance dried over concentrated sulphuric acid gave 15.81 cc. N at 21° and 763 mm.

	Calculated for $C_{20}H_{14}O_3N_2$ .	Found.
N	8.48	8.69

This compound crystallizes from dilute alcohol in white needles melting at 113°–114° and dissolving easily in alcohol, ether, benzene or hot ligroin.



By boiling with alcoholic potash, the benzoyl group can be split off and on evaporating to dryness, acidifying and crystallizing from alcohol, the pyrazolone is obtained in the form of small rhombic plates melting at 177°.

*1-Phenyl-3-furyl-4-isonitroso-5-pyrazolone*,  

$$\begin{array}{c} \text{C}_4\text{H}_3\text{O.C}:\text{N} \\ | \\ \text{HONC.CO} \end{array} \text{NC}_6\text{H}_5$$
—This compound was obtained by adding to an acid solution of the pyrazolone in dilute alcohol dilute sodium nitrite until starch-potassium iodide paper indicated the presence of an excess of nitrous acid. A bright red precipitate of the nitroso body separates as the sodium nitrite is added. It dissolves readily in dilute alcohol on warming, but appears again on cooling as an amorphous precipitate. No trace of crystallization from solutions allowed to evaporate spontaneously could be detected under the microscope.

Analysis:

0.1961 gram of the substance dried *in vacuo* gave 27.30 cc. N at 21° and 772 mm.

	Calculated for $\text{C}_{13}\text{H}_9\text{O}_3\text{N}_3$ .	Found.
N	16.48	16.12

This substance is soluble in alcohol, benzene, methyl alcohol, ether, chloroform or acetone, insoluble in water. It has no sharp melting point, but begins to soften at about 170° and gradually melts until at 183°–184° it decomposes, giving off gas and becoming dark brown. It is very hygroscopic and must be weighed protected from the air. It gives the Liebermann reaction with phenol and concentrated sulphuric acid.

By treatment with zinc dust and acetic acid the red color is completely discharged. The colorless acetic acid solution gives with ferric chloride a deep purple color and on warming a purple precipitate. With benzaldehyde and salicylic aldehyde yellowish precipitates insoluble in water are obtained.

*1-Phenyl-3-furyl-4-benzylidene-5-pyrazolone*,  

$$\begin{array}{c} \text{C}_4\text{H}_3\text{O.C}:\text{N} \\ | \\ \text{C}_6\text{H}_5\text{CH}:\text{C.CO} \end{array} \text{NC}_6\text{H}_5$$
—This compound was obtained by

heating benzaldehyde with the pyrazolone in molecular proportions in an oil bath to  $150^{\circ}$ . The reaction began at about  $120^{\circ}$ , the color of the mixture becoming deep red and ebullition beginning; to complete it the temperature was raised to  $150^{\circ}$  and kept there until no more bubbles were given off, after which the reaction product was allowed to cool and dissolved in hot toluene, when, on cooling, the benzyldiene derivative separated in the form of red flakes, showing no trace whatever of crystallization.

Analysis:

0.2112 gram of the substance dried *in vacuo* gave 15.85 cc. N at  $22^{\circ}$  and 763 mm.

	Calculated for $C_{20}H_{14}O_2N_2$ .	Found.
N	8.91	8.53

The benzyldienepyrazolone is a reddish amorphous powder, insoluble in alcohol, ether, or benzene, readily soluble in hot toluene or in chloroform. Alkalies dissolve it with a pinkish color and on warming decompose it, giving off an odor of benzaldehyde. It is insoluble in hydrochloric acid, but in concentrated sulphuric acid it dissolves readily, forming a bright red solution. It decomposes at  $210^{\circ}$ – $212^{\circ}$ .

*1-Phenyl-3-furyl-4-azobenzene-5-pyrazolone,*

$$\begin{array}{c}
 C_4H_3O.C=N \\
 | \\
 C_6H_5N:NCH.CO
 \end{array}
 \begin{array}{l}
 \\
 \rangle
 \end{array}
 NC_6H_5.$$
 —To 2 grams of the pyrazolone in alkaline solution were added 0.8 gram of aniline, carefully diazotized with the required amount of sodium nitrite and hydrochloric acid. A brownish red paste separated from the solution at once and this was purified by repeated crystallizations from alcohol-benzene mixtures until the melting point was constant.

Analysis:

0.1539 gram of the substance gave 23.61 cc. N at  $21^{\circ}$ .8 and 754 mm.

	Calculated for $C_{19}H_{14}O_2N_4$ .	Found.
N	16.97	17.36

This azobenzene pyrazolone crystallizes in long, light red,

slender needles, with smaller crystals adhering to and growing from them. It melts at  $165^{\circ}$  to a thick liquid adhering to the sides of the melting-point tube in a way similar to that of the 3-furyl-4-azobenzenepyrazolone, and decomposes at  $205^{\circ}$ . It is readily soluble in benzene or ethyl acetate, slightly soluble in ether, ligroin, or alcohol, and insoluble in water.

1-Phenyl-3-furyl-4- $\beta$ -azonaphthalene-5-pyrazolone,

$$\begin{array}{c} \text{C}_4\text{H}_3\text{O.C}=\text{N} \\ | \\ \text{C}_{10}\text{H}_7\text{N}:\text{NCH.CO} \end{array} \text{NC}_6\text{H}_5$$
 —To 2 grams of the pyrazolone in alkaline solution was added a solution of 1.3 grams of  $\beta$ -aminonaphthalene diazotized with hydrochloric acid and sodium nitrite until a drop of the solution gave a blue color with starch potassium iodide paper. A heavy, rusty-brown precipitate separated at once, which was filtered off and crystallized from a mixture of alcohol and benzene until it had a constant melting point.

Analysis:

0.1549 gram of the substance, dried *in vacuo*, gave 20.18 cc. N at  $24^{\circ}.5$  and 749 mm.

	Calculated for $\text{C}_{20}\text{H}_{16}\text{O}_2\text{N}_4$ .	Found.
N	14.74	14.35

This compound crystallizes in small, deep red needles, melting at  $202^{\circ}$ – $203^{\circ}$  to a thick viscous liquid, adhering to the sides of the melting-point tube. It is soluble in hot benzene, slightly soluble in the cold solvent, as well as in ether or alcohol, but insoluble in water or ligroin.

The action of diazotized substituted anilines was also tried, but the compounds were not analyzed. Diazotized sulphanilic acid added to a solution of the pyrazolone in dilute sodium hydroxide gave an amorphous red precipitate, soluble in alcohol, glacial acetic acid or hot water, but insoluble in benzene or ligroin. From none of these solvents could a crystallized product be obtained. Diazotized *p*-nitraniline gave a deep red precipitate under the same conditions. This was insoluble in water, but soluble in alcohol. From a hot dilute alcohol solution it could be obtained as an amorphous red powder. *p*-Toluidine gave a brown amorphous product.

Several experiments were undertaken to obtain the furyl-chlorpyrazole by treating the pyrazolone with phosphorus oxychloride according to the method of Michaelis.<sup>1</sup> In the cold or at the temperature of the steam bath the phosphorus oxychloride is without action. Heated in a sealed tube to 150°, the mixture of oxychloride and pyrazolone gave a charred resinous mass from which no definite product could be obtained.

*1-Phenyl-2-methyl-3-furyl-5-pyrazolone.*—Attempts to obtain the free base in a pure condition were unsuccessful owing to the ease with which it deliquesces and afterward passes into a tarry mass which does not solidify even over phosphorus pentoxide *in vacuo*. The best that could be done was to separate it in the form of a light brown amorphous powder by adding ligroin to its solution in chloroform, prepared by decomposing a salt of the base with sodium hydroxide and extracting with chloroform the brown oil that separated. The extract was then dried over calcium chloride and to it an excess of dry ligroin was added, when the base was precipitated as a light brown mass of curds which, by quickly transferring to a piece of biscuit ware and placing in a desiccator with phosphorus pentoxide, was obtained in the form of a light brown powder. If exposed to the air for a few minutes, moisture was quickly absorbed and the powder became a light brown tar that could not be dried in a desiccator. If the chloroform solution was evaporated *in vacuo* over concentrated sulphuric acid a varnishlike residue was left behind. The solvents used in this precipitation should be absolutely dry. No satisfactory analysis of this substance was made. This was not necessary as its identity was established by the analysis of its salts, which crystallize readily.

*Hydriodide*,  $C_{14}H_{12}O_2N_2HI$ .—This substance, which formed the starting material for further work on the 1-phenyl-2-methyl-3-furyl-5-pyrazolone, was readily obtained by heating equal weights of the pyrazolone and methyl iodide together with a little methyl alcohol in a sealed tube to 90°–100° for about 2 hours. On opening the tube the dark red liquid

<sup>1</sup> Ber. d. chem. Ges., **31**, 2907; **32**, 2402.

formed in the reaction crystallized in long, flat, almost colorless needles which were dissolved in alcohol and the last traces of color removed by passing sulphur dioxide into the solution. A large volume of ether was then added and the precipitated hydriodide crystallized from a benzene-alcohol mixture.

The substance was dried *in vacuo* and analyzed:

I. 0.2045 gram of the substance gave 0.1283 gram of AgI.

II. 0.1968 gram of the substance gave 14.59 cc. N at 29°.0 and 766 mm.

	Calculated for $C_{14}H_{12}O_2N_2HI$ .	I.	Found.	II.
I	34.51	33.90		...
N	7.61	...		8.15

These results are as near as could be expected when the slight stability of the compound is considered.

The hydriodide crystallizes in long, flat, transparent needles, which are very unstable, turning rapidly to yellowish green and then to brown. It is very soluble in methyl or ethyl alcohols or hot chloroform, but insoluble in ether, toluene, benzene, or ligroin. When moistened with water, the crystals form oily drops. It crystallizes from acetonitrile in tufts of needles. When pure it melts at 192°–193° with decomposition.

*Hydrochloride*,  $C_{14}H_{12}O_2N_2HCl$ .—On decomposing the iodide with strong sodium hydroxide the free base was obtained in the form of a light brown oil, which was extracted with chloroform and the solution thus obtained dried carefully over calcium chloride and saturated with a dry hydrochloric acid gas. After a short time the solution became almost solid, the hydrochloride separating in the form of light brown needles, which were filtered off, washed with ether and crystallized from a benzene-alcohol mixture. Repeated crystallizations did not completely remove the brown color. The substance was dried for analysis *in vacuo*.<sup>1</sup>

I. 0.2469 gram of the substance gave 0.1283 gram AgCl.

II. 0.2032 gram of the substance gave 17.75 cc. N at 20°.5 and 766 mm.

<sup>1</sup> Seven combustions for carbon and hydrogen were made with this substance, but no consistent results could be obtained even by using a very long combustion tube filled with lead chromate and containing two reduced copper spirals and a long silver coil.



	Calculated for $C_{14}H_{12}O_2N_2HCl$ .	I.	Found. II.	III.
Cl	12.84	12.85	...	...
N	10.13	...	10.04	...

The hydrochloride crystallizes in light, buff-colored prisms perfectly transparent when seen under the microscope. It is much more stable than the iodide and melts with decomposition at  $197^{\circ}$ – $198^{\circ}$ . It is readily soluble in methyl or ethyl alcohol or hot chloroform, but insoluble in ether, benzene, or ligroin. Water hydrolyzes this substance to an oil in the same way that it does the iodide. With ferric chloride it gives a deep red color and with chlorplatonic acid a light orange, crystalline precipitate. With picric acid a yellow picrate is obtained and with nitrous acid a beautifully crystallizing green nitroso derivative changing to red in acid solutions.

*Hydrobromide*,  $C_{14}H_{12}O_2N_2HBr$ .—If instead of passing hydrochloric acid into the chloroform solution of the base, dry hydrobromic acid was used, the hydrobromide of the base was obtained in the form of small white crystals which were crystallized from chloroform until the melting point was constant. The substance was dried for analysis for two hours at  $90^{\circ}$ , then over phosphorus pentoxide *in vacuo*.

0.1795 gram of the substance gave 0.1040 gram AgBr.

	Calculated for $C_{14}H_{12}O_2N_2HBr$ .	Found.
Br	24.92	24.65

The hydrobromide crystallizes from alcohol-benzene mixtures in small rectangular plates, soluble in alcohol or hot chloroform, but insoluble in ether, benzene or water. It melts with decomposition at  $194^{\circ}$ .

*Picrate*,  $C_{14}H_{12}O_2N_2 \cdot HOC_6H_2(NO_2)_3$ .—On adding a solution of picric acid to an alcohol solution of the base a precipitate of yellow needles separated which was filtered off and crystallized from alcohol. The substance was dried for analysis *in vacuo*.

0.2035 gram of the substance gave 25.76 cc. N at  $11^{\circ}.2$  and 750 mm. pressure.



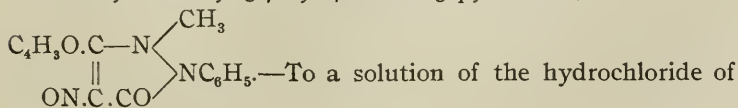
	Calculated for $C_{20}H_{15}O_6N_5$ .	Found.
N	14.93	14.87

The picrate consists of light yellow needles melting with decomposition at  $157^{\circ}$ – $158^{\circ}$ . It is soluble in hot alcohol, hot water, or warm benzene, but insoluble in ether or ligroin, and only slightly soluble in cold water.

*Synthesis of 1-Phenyl-2-methyl-3-furyl-5-pyrazolone.*

*Hydrochloride from Methylphenylhydrazine.*—To 1.5 grams of furoylacetic ester was added 0.7 gram of methylphenylhydrazine obtained by decomposing the oxalate with potassium hydroxide, extracting with ether and evaporating the dried extract until all the ether had boiled off. After heating 20 minutes on the steam bath no apparent action took place, as the mixture retained its fluidity. On heating on an oil bath at  $150^{\circ}$  the mixture began to boil after a short time, and the heating was continued until ebullition ceased, when, on cooling, the oil became very viscous but would not solidify. It was then dissolved in chloroform, dried with calcium chloride and saturated with dry hydrochloric acid. On adding ether a precipitate of light brown crystals separated which crystallized from ethyl acetate and a little alcohol in transparent prisms melting with decomposition at  $196^{\circ}$ – $197^{\circ}$ . The substance is very soluble in alcohol, slightly soluble in chloroform and hot ethyl acetate and insoluble in ether. Water hydrolyzed it to an oil. With nitrous acid in slightly acid solutions it gives a green, crystalline, nitroso derivative, which changes in strongly acid solution to a red compound, but can be changed to the green again by diluting or making alkaline. From the crystalline form, melting point, solubility and reaction with nitrous acid, it is evident that the substance obtained by the action of symmetrical methylphenylhydrazine on furoylacetic ester is identical with the hydrochloride of 1-phenyl-2-methyl-3-furyl-5-pyrazolone described above.

*1-Phenyl-2-methyl-3-furyl-4-nitroso-5-pyrazolone,*



1-phenyl-2-methyl-3-furyl-5-pyrazolone in dilute alcohol, hydrochloric acid and sodium nitrite were added; if an excess of hydrochloric acid was used a red compound separated, but if water was added to this or the amount of sodium nitrite was increased the precipitate became bright green and this green form was soon found to be the true nitroso derivative of the base, the red form being its hydrochloride. By crystallizing from dilute alcohol this substance was obtained pure. It was dried for analysis *in vacuo*.

0.1472 gram of the substance gave 20.42 cc. N at 22°.4 and 763 mm.

	Calculated for $C_{14}H_{11}O_3N_3$ .	Found.
N	15.61	15.74

This nitroso compound crystallized from dilute alcohol in glistening green needles melting at 185° with decomposition. It is soluble in hot alcohol, hot benzene, or hot water, but insoluble in the cold solvents and only very slightly soluble in ether. Acids turn it red, the green color being restored by alkalies or even on diluting with water. On standing with alkalies it is decomposed as shown below.

Four grams of the nitroso derivative were heated on the steam bath with a strong solution of caustic potash until all the nitroso derivative had disappeared and drops of a brown oil collected on the bottom of the dish; the liquid and oil were then transferred to a flask and distilled with steam until no more oil came over. This distillate, which reduced Fehling's solution readily, was extracted with ether, the extract dried over potassium hydroxide and the ether evaporated, leaving a yellow oil. To some of this in alcohol solution a few drops of dilute sulphuric acid were added, when, on scratching the vessel, a white precipitate of very small crystals separated which were washed with alcohol and ether and dried. Under the microscope they appeared as very small rectangular plates melting at 180° with decomposition. On adding oxalic acid, the oil was converted into the oxalate of methylphenylhydrazine, a white precipitate of very small needles.

Some of the oil was heated with mercuric oxide, when, it turned brown and a peculiarly disagreeable smell,

the same as that of diazomethylphenyl prepared from methylphenylhydrazine in a similar manner, was given off. From these reactions it is evident that the oil obtained by the breaking down of the nitroso derivative of 1-phenyl-2-methyl-3-furyl-5-pyrazolone is symmetrical methylphenylhydrazine, and that the methyl group of this pyrazolone is in the position we assigned to it.

*Hydrochloride*,  $C_{14}H_{11}O_3N_3HCl$ .—Into a hot alcohol solution of the nitroso derivative described above, gaseous hydrochloric acid was passed until a precipitate began to form. The color of the solution changed from green to red and on cooling small red needles were deposited which were washed with ether and dried for analysis *in vacuo* over caustic potash.

0.2075 gram of the substance gave 0.0949 gram  $AgCl$ .

	Calculated for $C_{14}H_{12}O_3N_3Cl$ .	Found.
Cl	11.62	11.31

The hydrochloride crystallizes in small bright red needles, but changes with extreme ease to the original green base. Even absolute alcohol effects the change unless a little hydrochloric acid is added to it. Once formed and kept perfectly dry, however, the hydrochloride is fairly stable. It decomposes at  $189^\circ$ .

*1-p-Bromphenyl-3-furyl-5-pyrazolone*,

$C_4H_3O.C=N$   
 $\begin{array}{c} | \\ H_2C.CO \end{array} \rangle NC_6H_4Br$ .—*p*-Bromphenylhydrazine reacts on the ester like phenylhydrazine. To 2 grams of the ester were added 2 grams of bromphenylhydrazine and the mixture heated on the oil bath to  $120^\circ$  for half an hour. The reaction product, a thick dark oil which on cooling solidified to a brown crystalline mass, was thoroughly washed with ether. This left a white powder which was crystallized from benzene-ligroin. It was dried for analysis *in vacuo*.

I. 0.1942 gram substance gave 0.1178 gram  $AgBr$ .

II. 0.1718 gram substance gave 14 cc. N at  $21^\circ.8$  and 767 mm. pressure.

	Calculated for $C_{12}H_9O_2N_2Br$ .	Found.
Br	26.23	25.81
N	9.18	9.33

This pyrazolone crystallizes in small white needles melting at  $160^{\circ}$ – $161^{\circ}$ . It is soluble in hot benzene or warm alcohol, but insoluble in ether, ligroin or water. Alkalies dissolve it readily and from their solutions it may be thrown down by acidifying; strong acids do not dissolve it. With nitrous acid it gives a red nitroso derivative and with ferric chloride a green precipitate.

*1-p-Sulphonylphenyl-3-furyl-5-pyrazolone*.—The free *p*-sulphonylphenylhydrazine does not react with the ester readily, but its sodium salt, on the contrary, behaves like all the other free hydrazines. Equal weights of the ester and sodium hydrazine-*p*-sulphonate prepared according to the method of Gallinek and von Richter<sup>1</sup> were heated on an oil bath to  $170^{\circ}$ , until the pasty mass at first formed was completely solidified. This product, the sodium salt of the pyrazolone, was washed with ether to remove any excess of ester, dissolved in water and acidified with dilute sulphuric acid, when a precipitate of brownish needles separated, which was filtered and crystallized from water after boiling with boneblack to remove the color.

I. 0.4005 gram of the substance, dried at  $90^{\circ}$  for 2 hours, lost 0.0210 gram when dried at  $130^{\circ}$ – $140^{\circ}$ .

II. 0.2515 gram of the substance, dried *in vacuo*, gave 0.1795 gram  $BaSO_4$ .

	Calculated for $C_{12}H_9O_2N_2SO_2H.H_2O$ .	Found.
H <sub>2</sub> O	5.56	5.24
S	9.87	9.80

This pyrazolone crystallizes from water in small square plates, which turn brown on standing. It is slightly soluble in hot alcohol and insoluble in ether, benzene, or chloroform. With nitrous acid it gives a red color, but does not give the "pyrazole blue" reaction. Alkalies dissolve it readily and from its alkaline solution it is reprecipitated by acids. It blackens but does not melt at  $295^{\circ}$ .

<sup>1</sup> Ber. d. chem. Ges., 18, 3172.

see errata  
p. 596

*1-m-Nitrophenyl-3-furyl-5-pyrazolone*,  

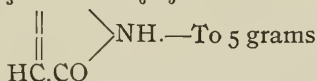
$$\begin{array}{c} \text{C}_4\text{H}_3\text{O.C}=\text{N} \\ | \\ \text{H}_2\text{C.CO} \end{array} \rangle \text{NC}_6\text{H}_4\text{NO}_2. — m\text{-Nitrophenylhydrazine reacted}$$
on the ester like other hydrazines. Two grams of the ester were heated in an oil bath with 1.6 grams of *m*-nitrophenylhydrazine. After heating one hour, the mixture had completely solidified to a brown mass which was washed with ether and crystallized from a benzene-ligroin mixture. It was dried *in vacuo* for analysis:

0.1701 gram of the substance gave 22.05 cc. N at 11°.4 and 766 mm.

	Calculated for $\text{C}_{13}\text{H}_9\text{O}_4\text{N}_3$ .	Found.
N	15.49	15.55

This pyrazolone crystallizes in small, thick, yellowish brown prisms, which are the prevailing form if the solution is kept perfectly quiet; if the crystallizing solution is stirred foliated crystals are obtained. The melting point is 174°–175°. The substance is soluble in hot benzene or hot alcohol, but insoluble in the cold solvents or in ether, ligroin or water. Sodium hydroxide dissolves it on warming; hydrochloric acid does not dissolve it. With ferric chloride a greenish brown color is obtained and with nitrous acid a red solution.

*1-Phenyl-5-furyl-3-pyrazolone*,  $\text{C}_4\text{H}_3\text{OC}=\text{N}-\text{C}_6\text{H}_5$



of the ester mixed with 4.2 grams of symmetrical acetphenylhydrazide were added 6 grams of phosphorus trichloride in small portions and the mixture was heated on a steam bath until the reaction was completed, which could be ascertained by the cessation of the evolution of hydrochloric acid. The reaction product, a thick purplish red syrup, was poured into strong ammonia when a dark oil separated out. The solution was extracted with ether and made barely acid when a precipitate of brown flakes was formed. This was filtered off and crystallized from 60 per cent. alcohol until it had a constant melting point. The yield was small,



amounting to only 0.5 gram of the pure product. The substance was dried *in vacuo*.

I. 0.2071 gram gave 0.5241 gram  $\text{CO}_2$  and 0.0821 gram  $\text{H}_2\text{O}$ .

II. 0.2086 gram gave 22.51 cc. N at  $23^\circ.5$  and 772 mm.

	Calculated for $\text{C}_{13}\text{H}_{10}\text{O}_2\text{N}_2$ .	I.	Found.	II.
C	69.03	69.01		...
H	4.42	4.40		...
N	12.39	...		12.31

This pyrazolone crystallizes in long, transparent prisms with square ends, which melt at  $176^\circ$ . It is slightly soluble in cold alcohol, readily in the warm solvent, fairly soluble in ether or in cold benzene, but insoluble in hot or cold water. Alkalies and concentrated acids dissolve it readily. With nitrous acid it gives a green nitroso derivative, but it does not give the "pyrazole blue" reaction.

The nitroso derivative was prepared by adding sodium nitrite to a hydrochloric acid solution of the pyrazolone. The color, which is at first orange, rapidly turns green and green flakes separate. The precipitate is fairly soluble in cold water and is turned red by acids.

#### SUMMARY.

The results of this research may be summarized as follows:

1. The properties and reactions of furoylacetic ester have been studied and show that this ester behaves like benzoyl- and acetacetic esters in most of its reactions. A new method for the synthesis of the ester has been tried and found to give better yields than the one previously used.

2. The action of hydroxylamine on the ester has been shown to take place in accordance with Abegg's theory and contrary to Hantzsch's views.

3. The 3- and 5-pyrazolone derivatives of furoylacetic ester have been studied and shown to give the usual reactions of the pyrazolones except as to the "pyrazole blue" reaction. A new homologue of antipyrine has been synthesized.



We are indebted to the Cyrus Warren Fund for some of the materials used in this research, for which we wish to express our gratitude.

Thanks are also due to Professor Charles Loring Jackson for his kindness in revising the manuscript.

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### ADDITIVE POWER OF 2-PENTENE.

BY ROGER F. BRUNEL AND EUGENE G. PROBECK.

Facts have long been known which showed that a wide difference exists in the additive power toward acids of the hydrocarbons of the ethylene series. This subject was recently discussed from the standpoint of the theories of Michael.<sup>1</sup> It was shown that with a certain member of the series, isobutene, a maximum additive power is observed, and the occurrence of this maximum, as well as the differences in additive power of those members examined, was explained from a theoretical standpoint.

These differences in the additive power of the unsaturated C : C group must, obviously, be due to the number and position of the other atoms in the molecule. Comparison of a large number of compounds of the aliphatic series led Michael to the adoption of the following hypothesis<sup>2</sup> regarding the relation between the position of the atoms and their influence on each other: The atom under discussion, in the above case one of the unsaturated carbon atoms, is numbered one, and the others then numbered according to their degree of removal as the various chains of atoms are followed out. The mutual influence between atom number 1 and the various other atoms of the molecule will then decrease according to the following scale:

$$2-3-5-6-4-7-(9-10-11)-8.$$

It is to be emphasized that the influence of an atom in position 2 or 3 is much greater than that of a similar atom less

<sup>1</sup> Michael and Brunel: *THIS JOURNAL*, **41**, 118 (1909).

<sup>2</sup> *J. prakt. Chem.*, N. F., **60**, 335.

closely connected. It appears that the relative importance of the different positions is correctly represented by this scale, as it has been found to apply not only in the case of the alkenes, but in many other cases examined by Michael.<sup>1</sup> This is true, however, only as regards their position; the value of atoms in the various positions could be expressed quantitatively only roughly. It would plainly be of interest to determine their value exactly for some class of compounds, and with this object in view one of the authors has undertaken the examination of the additive power of some hydrocarbons not dealt with in the former article. The end can, of course, be reached only by the comparison of a considerable number of compounds. The hydrocarbon so far examined is 2-pentene,  $\text{H}_3\text{CCH}:\text{CHCH}_2\text{CH}_3$ , which is simply related to trimethylethylene and to 1-butene, with which it has been compared.

Since the addition of a compound consisting of two different atoms or groups to 2-pentene may give rise to two different compounds it is first necessary to determine which of these is chiefly formed. This question was investigated by Wagner and Saytzeff.<sup>2</sup> The hydrocarbon was treated with hydriodic acid, the product converted into alcohol, and this oxidized to the ketone, which was shown to consist, largely, at least, of methylpropyl ketone. From theoretical considerations we may conclude that this should be the chief product, while a small amount of the diethyl derivative probably formed would have escaped detection by their method. An examination of the formula will show what results should be expected.

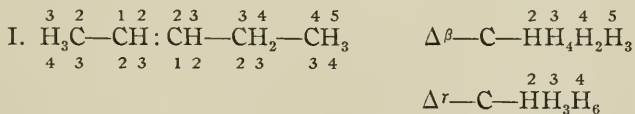
Certain assumptions underlying the entire argument must first be recalled. The compound which is added to the hydrocarbon is in all cases an acid or water, which can be represented by  $\text{HX}$ , the halogen acids being a typical example. The relative attraction of the two carbon atoms for H and X will determine which of the two possible products will be formed, and any difference in the affinity of these two

<sup>1</sup> Ber. d. chem. Ges., **39**, 2138-2195, and in various other articles as well.

<sup>2</sup> Ann. Chem. (Liebig), **179**, 313 (1876).

carbon atoms must be the result of the influence of the atoms in the molecule. The hydrogen atoms are probably the chief factor, and in view of the strong affinity of hydrogen for negative radicals, Br, SO<sub>4</sub>, OH, etc., we should expect that carbon atom to have the strongest attraction for the radical X which is most under the influence of the hydrogen atoms of the molecule; this carbon atom will have correspondingly less tendency to combine with another hydrogen atom. The question as to which of the two possible isomeric products will be formed is therefore to be settled by summing up the influences of the hydrogen atoms on the two unsaturated carbon atoms in the light of the above scale. This process consists merely of adding together the numbers of hydrogen atoms in the positions 2, 3, 4, etc., with respect to each of the carbon atoms.

The result of the application of this process to 2-pentene is as follows:



The figure above or below each letter indicates the position and the one at the right the number of atoms in that position. Removing from each list the atoms common to both we obtain:  $\Delta^\beta - \text{C} - \overset{3}{\text{H}}\overset{5}{\text{H}}$ ,  $\Delta^\gamma - \text{C} - \overset{4}{\text{H}}$ . It thus appears, after eliminating influences which are the same toward both unsaturated carbon atoms, that with respect to the  $\gamma$ -carbon atom there are four hydrogen atoms in position 4, while with respect to the  $\beta$ -carbon atom they are in positions 3 and 5. As a result the  $\beta$ -carbon atom will show a markedly greater affinity for the negative radical,<sup>1</sup> and correspondingly less for the hydrogen. The chief product will therefore be the compound  $\text{H}_3\text{CCH}_2\text{CH}_2\text{CHXCH}_3$  (to the extent, perhaps, of 70-80 per cent.). We shall estimate the rate of addition on

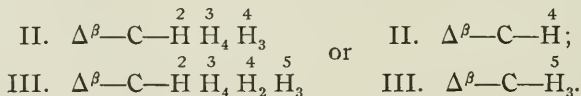
<sup>1</sup> Whether the negative radical is drawn toward this point in the molecule because the force exerted by this carbon atom upon it is actually greater, or whether it is due to the force exerted by the hydrogen atoms themselves toward it, is probably open to question. The result here is the same from either point of view, and the above manner of expression appears to be best in accordance with the facts.

the basis of the formation of this only. Since a certain amount of the other product,  $\text{CH}_3\text{CH}_2\text{CHXCH}_2\text{CH}_3$ , is being formed simultaneously, the rate of addition will always be a little greater than it would be if all the hydrocarbon had to be disposed of through formation of the former product, and this must be kept in mind.

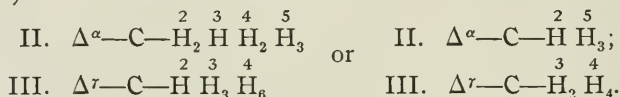
Assuming, then, that a 2-substituted normal pentane is to be the chief product, we may compare this hydrocarbon with 1-butene to see in which the addition should occur most readily, estimating first the force which will be exerted toward the negative group by that carbon atom with which it is to unite, then that toward the hydrogen. In the case of 1-butene the secondary derivative is practically the only product formed.<sup>1</sup>



By the addition process explained above we can compare the  $\Delta^\beta$ -carbon of (II) with the  $\Delta^\beta$ -carbon of (III) as follows:



Comparing the  $\Delta^\alpha$ -carbon of (II) with the  $\Delta^\gamma$ -carbon of (III):



The first comparison indicates that the attraction for the negative group will be greater in the butene than in the pentene, due to the presence of three hydrogen atoms in the position 5 as against one in the position 4 in the butene. In considering the attraction for the hydrogen atom we must take into account the facts presented in the paper of Michael and Brunel<sup>2</sup> pertaining to the occurrence of a maximum in additive power with isobutene. The presence of hydrogen atoms in

<sup>1</sup> Lieben and Rossi: *Ann. Chem. (Liebig)*, **158**, 166 (1871). A. and M. Saytzeff: *J. prakt. Chem., N. F.*, **3**, 88.

<sup>2</sup> *This Journal*, **41**, 118 (1909).

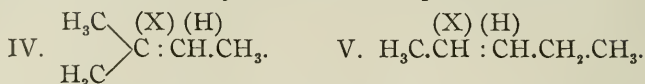
the molecule increases the attraction of the unsaturated carbon atoms for the negative part of the addendum, but at the same time decreases it for the hydrogen. It is evident that the former factor is the controlling one in the lower members, where the additive power increases with the number of carbon and hydrogen atoms, but that as the size of the molecule increases the latter factor predominates. After passing beyond isobutene, although the affinity for negative atoms such as the halogens undoubtedly increases, as shown by the avidity with which halogen addition products are formed, the tendency to add halogen acids or sulphuric acid may be expected to decrease, as previously shown by our experiments. This does not mean that any amylene will react less readily than any butene. Isobutene reacts the most readily of the alkenes, but if trimethylethylene is compared with pseudobutene the greater reactivity is shown by the former, in which the conditions are especially favorable to addition; and the expected decrease would then appear in the next step to the hexene series. We may say, however, that beyond the butene series any alkene is likely to form addition products with acids less readily than a member of the next lower series unless, through its structure, it offers conditions *much more* favorable for the addition than does the other.

In 2-pentene the attraction for the negative group is considerably greater than in 1-butene, as shown above. The attraction for hydrogen is also, as shown, somewhat less, although the difference here appears to be smaller than the former one, so that, from this consideration alone, we should look for greater additive power in the pentene, although the difference should not be great. If, however, we bear in mind the fact that with the transition from the  $C_4$  to the  $C_5$  series the relative importance of the latter factor, the reduction in the affinity for hydrogen, increases, it will appear quite possible that the amylene should show the weaker additive power, as has been found to be the case, the ratio butene:amylene being about 7:5.

The comparison of 2-pentene with trimethylethylene is also



of interest. In the formulas the predominant course of the addition is indicated by the letters in parentheses.



An examination of these formulas will show that the carbon atoms which combine with hydrogen are subject to the same influence in the two cases, the numbers of hydrogen atoms in the various positions being identical. All of the difference in additive power must then lie in the degree of attraction for the negative radical. This difference is caused chiefly by a change in the position of one methyl group. In (IV) it is in position 2,3 with respect to the carbon atom which unites with the negative group, while in (V) it is in position 4,5. The only other difference is the removal of a hydrogen atom from position 4 in (IV) to position 2 in (V). These two factors are in opposition to each other, but the first is the greater, and the results of this comparison should give us, for this particular case at least, an estimate of the relative values or influences of hydrogen atoms in the positions 3 and 5. The difference appears to be considerable, as the velocity with which trimethylethylene dissolves in dilute sulphuric acid is over one hundred times as great as for 2-pentene.

It is obvious that this method of comparing the hydrocarbons is open to the objection that in the heterogeneous system with which we are dealing differences in the merely physical solubility of the hydrocarbons in the aqueous acids used would exert great influence on the results. It does not appear that these differences should be very great, and, even if they were the chief factor, these great differences in solubility with such small changes in structure would be of little less interest than differences in reactivity toward the acids used. One of the authors intends to examine, in the near future, the solubility in water of some of the hydrocarbons used.

#### EXPERIMENTAL PART.

*Diethylcarbinol* was prepared according to the Grignard method. One hundred and nine grams ethyl bromide were



added to 24 grams magnesium in anhydrous ether. The ethyl bromide was added as fast as possible, the flask, after the reaction had begun, being placed in a mixture of ice and salt and shaken continuously. A few minutes' heating nearly completed the solution of the magnesium. Thirty-eight grams ethyl formate were then added, and the whole was allowed to stand an hour, then boiled thirty minutes and worked up in the usual manner. The product was dried with potassium carbonate and fractionated with a short column of beads. Seventeen grams were obtained distilling at  $112^{\circ}$ – $113^{\circ}$ , and 11.5 grams at  $113^{\circ}$ – $113^{\circ}.5$ , these together making a yield of 63 per cent.<sup>1</sup>

*Diethylcarbinyl iodide* was prepared by passing hydriodic acid gas into the carbinol at  $0^{\circ}$ . When the saturated solution was allowed to come to room temperature two layers were formed, the upper of which was washed with carbonate, dried, and fractionated. Nineteen and eight-tenths grams were obtained boiling at  $142^{\circ}$ – $144^{\circ}$  and 40.3 grams at  $144^{\circ}$ – $146^{\circ}$ .

*2-Pentene* was prepared by the method of Wagner and Saytzeff<sup>2</sup> by treating the iodide with alcoholic potash and distilling off the low-boiling product. From 60 grams of iodide 17.5 grams of hydrocarbon were obtained. After two fractionations with beads 13.2 grams were obtained boiling at  $37^{\circ}$ – $39^{\circ}$ .

*1-Butene* was prepared by the method described by Butlerow<sup>3</sup> for isobutene, the yield, as already noted, being poor.

*Comparison of 2-Pentene and 1-Butene.*—1-Butene, boiling at  $-5^{\circ}$ , was condensed and sealed in a tube with 1 cc. of dilute sulphuric acid, the amount being determined by weighing before and after its introduction, and an equal amount of the amylene was then sealed in a similar tube. In the table below, in the last column, are given the times that would have been required for solution of the butene if equimolecular amounts of the two had been taken.

<sup>1</sup> More recently yields of 75–80 per cent. have been obtained. An excess of 5–10 per cent. of ethyl bromide is usually added to complete the solution of the magnesium as quickly as possible.

<sup>2</sup> Ann. Chem. (Liebig), **175**, 373 (1875).

<sup>3</sup> Z. Chem., **13**, 238 and 544 (1870). Ber. d. chem. Ges., **3**, 622 (1871).

Pts. acid to 1 pt. water.	Wt. of hydro- carbon. Gram.	Time of solution of		Time for 1-butene with equimol. amount. Minutes.
		2-Pentene. Minutes.	1-Butene. Minutes.	
3.0	0.0319	135	121	97
3.5	0.0342	130	118	94

The additive powers of 2-pentene and 1-butene are therefore nearly in the ratio of 5:7.

*Comparison of 2-Pentene and Trimethylethylene.*—Small sealed tubes were prepared, each containing 0.040 gram of hydrocarbon and a large excess of dilute sulphuric acid. These were placed on the shaking machine and the time required for complete solution of the hydrocarbon noted. The results are given in the following table:

Mols. of H <sub>2</sub> SO <sub>4</sub> to one of hydrocarbon.	Parts of acid to one part of water.	Time of solution	
		Amylene.	Trimethylethylene.
15	1.5	Not dissolved after 23 hours	10 mins.
15	2.0	7 hrs. 54 min.	At once
15	3.0	2 hrs. 17 min.	At once
15	3.5	2 hrs. 8 min.	At once

[Contributions from the Chemical Laboratory of Harvard College.]

## A METHOD FOR PURIFYING AND DRYING ORGANIC LIQUIDS BY WIPING.

BY C. LORING JACKSON AND A. H. FISKE.

In the course of a research on curcumine, carried on by Dr. Latham Clarke and one of us, it became necessary to determine the nature of 2 or 3 drops of an organic oil, which was obtained mixed with hydriodic acid. As there was too little to dry and distil in the ordinary way, and, owing to its volatility, we were afraid to dry it in a desiccator, we were obliged to find some other method for bringing it into a state fit for analysis, and hit upon the plan of drying it by wiping with strips of moist filter paper, after the hydriodic acid had been removed by washing. This method seemed to work so well that we decided to test it by further experiments, and now describe it for the benefit of others who, like us, have not found

in the literature any way of dealing with a case like this. We selected as the substance for our experiments commercial chloroform, which gave the following results on analysis:

- I. 0.2041 gram substance gave 0.7263 gram AgCl.  
 II. 0.1783 gram substance gave 0.6335 gram AgCl.

	Calculated for CHCl <sub>3</sub> .	I.	Found. II.
Cl	89.13	87.98	87.86

It therefore contained a slight amount of impurity, probably water or alcohol.

In our first experiment, 0.2256 gram of this chloroform was washed with 0.1284 gram of water, which was shaken with it. Part of the water was then removed with a small pipette, and the rest with strips of filter paper about 5 mm. wide and creased lengthwise, so as to make them stiffer and easier to handle; these were moistened with water sufficiently to make them repel the chloroform, but were kept still dry enough to take up more water. The inside of the tube, both above and below the liquid, was wiped with these strips of paper until it seemed perfectly dry, and the chloroform was then analyzed (I) without any other drying. The chloroform lost during this treatment 0.0748 gram, or about 33 per cent. A second specimen (II) weighing 0.3023 gram, treated in the same way, lost 0.0854 gram, or about 28 per cent.

- I. 0.1508 gram substance gave 0.5423 gram AgCl.  
 II. 0.2169 gram substance gave 0.7781 gram AgCl.

	Calculated for CHCl <sub>3</sub> .	I.	Found. II.
Cl	89.13	88.92	88.69

These results show that the chloroform was dried sufficiently for all practical purposes by wiping it with slightly moist filter paper; and this conclusion is supported by the following analyses of volatile liquids obtained in the course of researches made in this laboratory, all of which were wiped in the manner described above.

0.2102 gram of methyl iodide obtained from curcumine gave 0.3454 gram AgI.

	Calculated for. $\text{CH}_3\text{I}$ .	Found.
I	89.43	88.84

I. 0.2943 gram of bromoform obtained in one of our researches gave 0.6560 gram AgBr.

II. 0.2391 gram gave 0.5339 gram AgBr.

	Calculated for $\text{CHBr}_3$ .	I.	Found.	II.
Br	94.86	94.88		94.99

The following experiments were tried to see whether a substance dissolved in the chloroform could be removed to advantage by this method of wiping.

A. With 0.5193 gram of chloroform was mixed about 0.001 gram of iodine. After the iodine had completely dissolved, slips of filter paper moistened with a solution of 2 grams of potassic iodide in 10 cc. of water were immersed in the liquid until it had become colorless. It was necessary to use 8 pieces of paper to remove the last trace of the color. A drop of water was then added and shaken with the chloroform, which was afterward wiped dry with strips of slightly moist filter paper. The loss in all these processes was 0.3410 gram, or about 66 per cent.

B. With 0.5316 gram of chloroform was mixed about 0.001 gram of iodine as before, and the mixture shaken with successive drops of the iodide of potassium solution until the color was discharged, the solution being removed with a very small pipette. Nine treatments with the potassic iodide solution were necessary before the color disappeared. The loss of chloroform was 0.2801 gram, or about 53 per cent. The colorless liquid was wiped dry.

A. 0.1783 gram gave 0.6397 gram AgCl.

B. 0.2515 gram gave 0.9108 gram AgCl.

	Calculated for $\text{CHCl}_3$ .	A.	Found.	B.
Cl	89.13	88.72		89.52

These analyses show that the wiping had removed all the dissolved iodine, whereas the washing was less efficient, a small amount of iodine or potassic iodide having been left in the

chloroform. The wiping was also more conveniently applied, and did its work completely in 8 applications, while the washing required 9 for only partial purification; on the other hand, the loss of chloroform was 60.9 milligrams greater with the wiping than with the washing.

It is obvious that a liquid cannot be dried completely by wiping it with slightly moist filter paper, but the experiments described show that the amount of water left in the substance is less than 0.5 per cent., and therefore usually not enough to interfere with the identification of the substance by analysis.

We feel justified in recommending this process for the purification and drying of the substance for analysis in the not uncommon cases where in an investigation it is necessary to determine the composition of a liquid obtained in too small quantity to be treated with a drying agent, followed by distillation, and too volatile to be dried to advantage *in vacuo*. One great point in its favor is that it takes only a few minutes instead of the hours needed for the older methods of drying; and in the case for which it was invented this rapidity of action was a great advantage, as the substance was decomposed by exposure to the air for 3 hours, so that here drying by wiping was not only more convenient, but also much safer, than the usual methods.

CAMBRIDGE, MASS.,  
June 18, 1910.

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[Contributions from the Sheffield Laboratory of Yale University.]

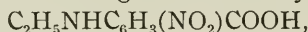
CLXXXIV.—ALKYLOLATION OF AROMATIC AMINO  
ACIDS: NITRAMINO AND IODAMINO ACIDS.

[FOURTH PAPER.]

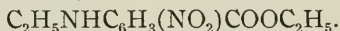
BY HENRY L. WHEELER AND CARL O. JOHNS.

We have now examined the behavior of 4-nitro-2-amino-benzoic acid (I), 4-amino-2-nitrobenzoic acid (II), 4-iod-2-aminobenzoic acid (IV), and 4,5-diiod-2-aminobenzoic acid (VI) when warmed with potassium hydroxide and an excess of alkyl iodide in alcoholic solution.

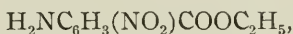
The silver salt of 4-nitro-2-aminobenzoic acid was found by Wheeler and Barnes<sup>1</sup> to give the *N*-alkyl compounds



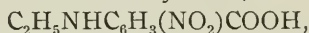
and, in smaller amount,



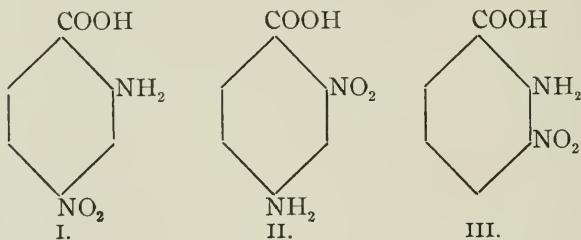
We find, with potassium hydroxide and ethyl iodide, that this acid gives a mixture of 40 per cent. of the primary amino ester,



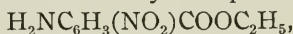
about 40 per cent. of the *N*-alkyl acid,



and 20 per cent. of unaltered acid. In other words, there appears to be about an equal tendency for the potassium salt of this acid to give *N*- and *O*-ethyl derivatives.



When 2-nitro-4-aminobenzoic acid (II) was treated in the same manner we obtained only the primary *O*-ester,



(43.4 per cent.) and the unaltered acid (48.3 per cent.). These results are precisely opposite to what would be expected from the theory of stereochemical interference, since 2-nitro-4-aminobenzoic acid should give a *N*-derivative more readily than 4-nitro-2-aminobenzoic acid, the latter acid having the carboxyl adjacent to the  $\text{—NH}_2$  group.

It appears that substituted *o*-aminobenzoic acids give *N*-derivatives more readily than the isomeric *p*-aminobenzoic acids; however, in this series the potassium salt of 3-nitro-2-aminobenzoic acid (III) gives an *O*-ester.<sup>2</sup>

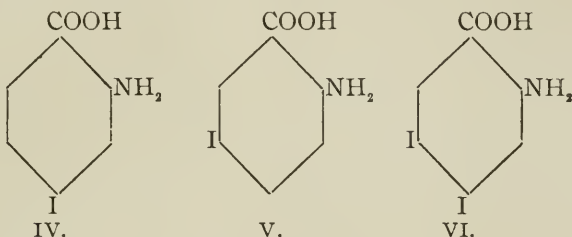
The influence of position and negative character of substit-

<sup>1</sup> THIS JOURNAL, 20, 217 (1898).

<sup>2</sup> Zacharias: J. prakt. Chem., 43, 437 (1891).



uents, in the absence of stereochemical interference, can now be compared in the following series: 4-Iod-*o*-aminobenzoic acid (IV), 5-Iod-*o*-aminobenzoic acid (V), and 4,5-diiod-*o*-aminobenzoic acid (VI).



Both 4-iod-*o*-aminobenzoic acid and 5-iod-*o*-aminobenzoic acid<sup>1</sup> gave 71–76 per cent. of *N*-alkyl acids and no *O*-esters were observed, while 4,5-diiod-*o*-aminobenzoic acid alkylated with difficulty and gave an *O*-ester (28 per cent.) along with unaltered acid.

Since 4,5-diiod-*o*-aminobenzoic acid gives an *O*-ester it is not necessarily due to stereochemical interference that 3,5-diiod-*p*-aminobenzoic acid<sup>2</sup> and especially 3,5-diiod-*o*-aminobenzoic acid<sup>3</sup> give esters and not *N*-derivatives by the above treatment.

These results show conclusively that the tendency of amino acids to react in an abnormal manner and give esters is not dependent on stereochemical interference.

#### EXPERIMENTAL PART.

*2-Amino-4-nitrobenzoic Acid.*—This acid was first prepared by Wheeler and Barnes.<sup>4</sup> We have improved the yield by the use of magnesium sulphate and by proceeding as follows: Thirty-five grams of 4-nitro-*o*-acetotoluide were suspended in a liter of hot water and 90 grams of crystallized magnesium sulphate were added. Steam was passed into this mixture, in a large bottle, and 90 grams of potassium permanganate in 2 liters of hot water were added in portions from time to

<sup>1</sup> Wheeler and Johns: *THIS JOURNAL*, **42**, 403 (1910).

<sup>2</sup> Wheeler and Liddle: *Ibid.*, **42**, 455 (1909).

<sup>3</sup> Wheeler and Johns: *Loc. cit.*

<sup>4</sup> *THIS JOURNAL*, **20**, 219 (1898).

time. The oxidation was complete in less than three hours. The manganese dioxide was then filtered off, well washed with hot water, and the total filtrates were evaporated to about 500 cc. The solution was made distinctly alkaline with ammonia and filtered. On acidifying with hydrochloric acid, a bulky precipitate of the acetamino acid separated. This was filtered off and dissolved in 200 cc. of alcohol containing 15 cc. of concentrated sulphuric acid. When this solution was digested on the steam bath the free acid separated as a bright, orange, crystalline precipitate. The yield, on diluting the solution with water, was 88 per cent. of the calculated. The acid melted at  $264^{\circ}$ , as previously described.

*Ethyl 2-amino-4-nitrobenzoate* was prepared by Wheeler and Barnes, but the melting point of the substance was not given.

We have prepared the ester by boiling the acid in alcoholic solution containing a little sulphuric acid. After evaporating most of the alcohol the residue was treated with dilute ammonia and crystallized from alcohol. It formed orange-colored prisms with rectangular ends and it melted to an oil at  $100^{\circ}$ . It was very soluble in ether and hot alcohol.

	Calculated for $C_9H_{10}O_4N_2$ .	Found.
N	13.33	13.27

*Action of Ethyl Iodide upon Potassium 2-Amino-4-nitrobenzoate.*—Five grams of the acid were dissolved in 75 cc. of alcohol containing 1.6 grams of potassium hydroxide (one molecule). To this 6 grams of ethyl iodide were added. The mixture was heated for 2 hours under a return condenser, whereupon the solution became acid to litmus. It was evaporated to dryness and the residue was treated with dilute ammonia. This left 2.3 grams of insoluble substance which, when crystallized from alcohol, resembled the oxygen ester above in every respect and when mixed with it the mixture melted sharply at  $100^{\circ}$ . The yield of ester was 40 per cent. of the calculated.

When the ammonia solution, obtained above, was acidified with hydrochloric acid it gave a precipitate which weighed 4.3 grams. This was a mixture of unaltered acid and the

*N*-ethyl acid. The unaltered acid was isolated by crystallizing from alcohol. It was identified by its melting point and the following analysis:

	Calculated for $C_7H_6O_4N_2$ .	Found.
N	15.38	15.16

The alcoholic mother liquors from which the unaltered acid had been isolated were concentrated and by fractional crystallization from alcohol the *N*-ethyl acid was isolated in the form of golden yellow plates. This substance was identical with the acid described by Wheeler and Barnes and when esterified it gave the ethyl ester melting at about  $80^\circ$ . It was impossible to get the exact yield of the *N*-ethyl acid, but it was estimated to be about 40 per cent. of the calculated.

	Calculated for $C_9H_{10}O_4N_2$ .	Found.
N	13.33	13.56

Attempts were made to introduce iodine into 4-nitranthranilic acid in the same manner as proved successful in the case of anthranilic acid, but it was found that after digesting the aqueous solution of the potassium salt with iodine on the steam bath the acid was recovered unaltered. An attempt to iodate the acid by means of iodine monochloride also failed.

*2-Iod-4-nitrobenzoic Acid*.—Eight grams of 2-amino-4-nitrobenzoic acid were dissolved in 100 cc. of 40 per cent. sulphuric acid and 4 grams of sodium nitrite were added to the cold solution. After a few minutes the mixture was poured on crushed ice, giving a clear solution. Ten grams of potassium iodide were added and the mixture was heated on the steam bath, the excess of iodine being removed by means of sodium bisulphite. The yield was 99 per cent. of the calculated.

The iodinitro acid was very soluble in ether, benzene, alcohol, chloroform or acetone and difficultly soluble in ligroin or carbon tetrachloride. It dissolved sparingly in hot water and separated on cooling partly as an oil that soon solidified and partly as long slender prisms which melted at  $143^\circ$ . Its solution in ammonia was precipitated by hydrochloric acid:

	Calculated for $C_7H_4O_4NI$ .	Found.
N	4.77	4.66

*2-Iod-4-aminobenzoic Acid*.—Two grams of 2-iod-4-nitrobenzoic acid were dissolved in 25 cc. of concentrated ammonia. This solution was mixed with one containing 12.2 grams of ferrous sulphate in 50 cc. of water. There was a slight evolution of heat and reduction took place rapidly. The mixture was heated on the steam bath and filtered after 5 minutes. The filtrate was evaporated to dryness and the residue extracted with alcohol. On evaporating the alcohol and treating with a little water, 73 per cent. of the calculated amount of the amino acid was obtained.

This iodamino acid was easily soluble in ether or alcohol and difficultly soluble in benzene, but dissolved slightly in hot water. It dissolved in dilute alkali and was precipitated by hydrochloric acid. When crystallized from dilute alcohol it formed colorless needles that effervesced at  $180^\circ$ :

	Calculated for $C_7H_4O_2NI$ .	Found.
N	5.32	5.22

When an attempt was made to iodate this acid by treating the material in glacial acetic acid with iodine monochloride, a dark solution resulted and when diluted with water and made alkaline with ammonia a black, sticky tar was obtained. This did not dissolve in alkali.

When the acid (2 grams) was treated with 4 molecular proportions of potassium hydroxide and 5 of ethyl iodide in alcoholic solution for 4 hours, an unpromising black tar was again obtained. This was not soluble in ammonia.

*2-Nitro-4-acetaminobenzoic Acid*.—This acid has recently been prepared by Bogert and Kropff<sup>1</sup> by nitrating *p*-toluidine, acetylating and oxidizing with potassium permanganate.

We started with 2,4-dinitrotoluene, partially reduced this with ammonium sulphide, acetylated and oxidized with potassium permanganate. The latter operation was carried out as described above in the case of the preparation of 2-amino-

<sup>1</sup> J. Am. Chem. Soc., **31**, 847 (1909).

4-nitrobenzoic acid. We can add to Bogert and Kropff's description that the best yield (74.2 per cent. of the calculated) of this acid was obtained when slightly less than three parts of potassium permanganate were used to one part of *o*-nitro-*p*-acettoluide.

The acid was soluble in alcohol and difficultly soluble in ether and boiling benzene. It was sparingly soluble in hot water, from which it crystallized in rectangular prisms. It melted to a brown oil at  $217^{\circ}$  with slight effervescence (Bogert and Kropff give  $219^{\circ}$ , corr.).

	Calculated for $C_9H_8O_5N_2$ .	Found.
N	12.50	12.33

*2-Nitro-4-aminobenzoic Acid*.—Attempts to hydrolyze off the acetyl group from the above by means of either concentrated or dilute hydrochloric acid resulted in the formation of considerable quantities of *m*-nitraniline, along with more or less of the acid.

Bogert and Kropff used dilute sulphuric acid to remove the acetyl group or, better, a 10 per cent. solution of potassium hydroxide.

The hydrolysis was readily accomplished by means of normal potassium hydroxide. Ten grams of the acetyl acid were heated, with 200 cc. normal potassium hydroxide solution for one hour on the steam bath. The solution was cooled and then carefully precipitated with hydrochloric acid. The yield was 87 per cent. of the calculated.

The acid was easily soluble in alcohol and difficultly soluble in ether or benzene. It was moderately soluble in hot and but slightly soluble in cold water. It crystallized from dilute alcohol in bronze-colored leaflets composed of small crystals that decomposed with charring and effervescence at  $232^{\circ}$ .

A patent (D. R. P. No. 204,884) for the preparation of this acid has recently been taken out by the firm of Meister Lucius and Brüning, their method being the partial reduction of 2,4-dinitrobenzoic acid. The melting point  $234^{\circ}$ – $235^{\circ}$  is given, while Bogert and Kropff give  $239^{\circ}.5$  (corr.).

	Calculated for $C_7H_5O_4N_2$ .	Found.
N	15.38	15.25

*Action of Ethyl Iodide upon Potassium 2-Nitro-4-aminobenzoate.*

*Ethyl 2-Nitro-4-aminobenzoate.*—Twelve grams of *o*-nitro-*p*-aminobenzoic acid were dissolved in 200 cc. of alcohol containing 5 grams of potassium hydroxide, and 25 grams of ethyl iodide were added. The mixture was heated on the steam bath under a return condenser. The sodium salt separated and slowly dissolved again. The heating was continued for 5 hours, and after evaporating to dryness the residue was treated with water to remove potassium salts. This filtrate gave 3.3 grams of unaltered acid when acidified with hydrochloric acid. The portion not soluble in water was treated with dilute ammonia and 2.5 grams of unaltered acid were obtained on acidifying. The portion insoluble in ammonia weighed 6.0 grams, or 43 per cent. of the calculated. This was the ethyl ester. When crystallized from dilute alcohol it formed stout, elongated prisms, which melted at  $130^\circ$ . It was easily soluble in cold alcohol, ether and benzene, but almost insoluble in hot water.

	Calculated for $C_9H_{10}O_4N_2$ .	Found.
N	13.33	13.46

The above ester was also formed by heating 10 grams of *o*-nitro-*p*-aminobenzoic acid in 120 cc. of absolute alcohol containing 2 cc. of sulphuric acid for 10 hours on the steam bath. Only 3.5 grams of ester were formed, which is 30.4 per cent. of the calculated yield. One and five-tenths grams of *m*-nitraniline were formed and 4 grams of unaltered acid were recovered.

*2-Nitro-4-iodbenzoic Acid.*—Ten grams of *o*-nitro-*p*-aminobenzoic acid were dissolved in 30 cc. of concentrated sulphuric acid. This was best accomplished by grinding the mixture in a mortar. Four and two-tenths grams of sodium nitrite were added and the mixture was poured on crushed ice, whereupon the whole dissolved to a clear yellow solution, which was added to an aqueous solution of 25 grams of potas-



sium iodide. A bulky, spongy, black mass was formed which soon hardened to a red powder. The mixture was warmed and the free iodine was removed with sodium bisulphite. The yield of crude material was 13 grams, or 81 per cent. of the calculated.

When crystallized from dilute alcohol the acid gave beautiful, diamond-shaped prisms, which melted to a clear oil at  $192^{\circ}$ . It was easily soluble in ether and alcohol, moderately soluble in boiling benzene, and almost insoluble in hot water.

	Calculated for $C_7H_4O_4NI$ .	Found.
I	43.34	42.87
N	4.77	4.70

*2-Amino-4-iodbenzoic Acid*.—Eight grams of *o*-nitro-*p*-iodbenzoic acid were dissolved in 100 cc. of concentrated ammonia and 50 grams of ferrous sulphate dissolved in 200 cc. of water were added to this solution. After remaining for one hour the mixture was heated for 15 minutes on the steam bath and then filtered. The ferric hydroxide was washed with water and on evaporating the filtrates and precipitating with hydrochloric acid the yield of iodamino acid obtained was 89 per cent. of the calculated. The acid was easily soluble in cold alcohol or ether, difficultly soluble in benzene, and almost insoluble in water. When crystallized from dilute alcohol it formed colorless, flat prisms, pointed at both ends. It decomposed with charring at  $208^{\circ}$ .

	Calculated for $C_7H_6O_2NI$ .	Found.
I	48.29	48.15

*Action of Ethyl Iodide upon Potassium 2-Amino-4-iodbenzoate.*

*2-Ethylamino-4-iodbenzoic Acid*.—Four grams of the above acid were dissolved in 40 cc. of 93 per cent. alcohol containing 0.9 gram of potassium hydroxide. Ten grams of ethyl iodide were added and the solution was heated on the steam bath for 1 hour and then evaporated to dryness. The solid residue was not soluble in water. It dissolved in dilute ammonia and when acidified with hydrochloric acid the precipitate obtained weighed 3.2 grams, or 72 per cent. of that calculated

for a *N*-ethylamino acid. It was easily soluble in ether or benzene, almost insoluble in hot water, and easily soluble in hot alcohol. It crystallized from alcohol in clusters of plates, which melted with effervescence at 188°.

	Calculated for $C_9H_{10}O_2NI$ .	Found.
I	43.65	43.03

*Action of Methyl Iodide upon Potassium 2-Amino-4-iodbenzoate.*

*2-Methylamino-4-iodbenzoic Acid.*—Four grams of 2-amino-4-iodbenzoic acid were dissolved in 50 cc. of alcohol containing 0.9 gram of potassium hydroxide. Seven grams of methyl iodide were added and the mixture was heated for 1 hour under a return condenser, after which it was evaporated to dryness. The potassium iodide was dissolved out with water and the solution thus obtained gave no precipitate when acidified. There was therefore no potassium salt of the acid unacted upon. The portion insoluble in water dissolved readily in dilute ammonia and when precipitated with hydrochloric acid weighed 3.2 grams, or 76 per cent. of the calculated. The acid was easily soluble in ether or benzene and almost insoluble in boiling water. It was purified by dissolving in ether and filtering off a trace of black substance. The ether solution was evaporated to dryness and the residue was crystallized from alcohol. It then formed a bulky mass of needles that melted to an oil at 197°.

	Calculated for $C_8H_8O_2NI$ .	Found.
I	45.84	45.83

*2-Amino-4,5-diiodbenzoic Acid.*—Five grams of 2-amino-4-iodbenzoic acid were dissolved in 75 cc. of water containing 1.5 grams of potassium hydroxide and 5 grams of powdered iodine were added. The mixture was shaken until practically all of the iodine had dissolved and a gray precipitate appeared. The excess of iodine was removed with sodium bisulphite and the precipitate filtered off. It weighed 6 grams, or 81 per cent. of the calculated.

This acid was readily soluble in ether or alcohol, moderately soluble in boiling benzene, and almost insoluble in hot water.

After treatment with ether a small amount of black substance could be removed by filtering. The solution was then evaporated to dryness and the residue was dissolved in 14 per cent. ammonia by warming. On cooling, the ammonium salt separated in clusters of colorless, pointed prisms. When the salt was dissolved in very dilute ammonia and the solution was acidified with hydrochloric acid, a white crystalline precipitate was obtained. This did not have a definite melting point but began to give off iodine above  $200^{\circ}$ , turning black and effervescing slightly at  $210^{\circ}$ – $220^{\circ}$ .

I	Calculated for	Found.
	$C_7H_5O_2NI_2$ .	
	65.23	65.03

*3,4-Diiodbenzoic Acid*.—Two grams of the above amino acid were dissolved in 50 cc. of alcohol containing 2 cc. of sulphuric acid. Two grams of sodium nitrite were added and the mixture was heated for a half hour on the steam bath. The resulting solution, on pouring into water, gave a bulky precipitate. This melted at about  $255^{\circ}$ , when crystallized from alcohol, and when mixed with a sample of 3,4-diiodbenzoic acid prepared by Wheeler and Liddle<sup>1</sup> the melting point was not altered.

*2,4,5-Triiodbenzoic Acid*.—Two grams of 2-amino-4,5-diiodbenzoic acid were dissolved in 20 cc. of concentrated sulphuric acid, the solution was cooled and 1.0 gram of sodium nitrite was added. This mixture was poured on cracked ice which had been moistened with concentrated hydrochloric acid. After the lapse of an hour the undissolved portion was filtered off and an aqueous solution of 5 grams of potassium iodide was added to the filtrate. A violent reaction ensued. After heating for a short time on the steam bath the excess of iodine was removed with sodium bisulphite and the triiod acid then appeared as a brick-red deposit. The pure acid was almost insoluble in hot water or benzene, moderately soluble in ether or hot alcohol. From the latter solvent it crystallized in small, colorless needles, which melted to an oil at  $248^{\circ}$ . The yield was 72 per cent. of the calculated.

<sup>1</sup> THIS JOURNAL, 42, 457 (1909).

	Calculated for $C_7H_3O_2I_3$ .	Found.
I	76.20	75.90

*Action of Ethyl Iodide upon Potassium 2-Amino-4,5-diiodbenzoate.*

*Ethyl 2-Amino-4,5-diiodbenzoate.*—Two grams of 2-amino-4,5-diiodbenzoic acid were dissolved in 40 cc. of absolute alcohol containing 0.3 gram of potassium hydroxide. Two grams of ethyl iodide were added and the mixture was heated for one hour on a steam bath, at the end of which time it was acid to litmus. On evaporating to dryness and treating the residue with dilute ammonia 0.6 gram, or 28 per cent., of the calculated amount of ester remained undissolved. This was almost insoluble in hot water, but dissolved readily in ether or benzene, and was easily soluble in hot alcohol, from which it crystallized in slender prisms which melted to an oil at  $137^\circ$ . When warmed with dilute alkali it gave 2-amino-4,5-diiodbenzoic acid.

	Calculated for $C_9H_9O_2NI_2$ .	Found.
I	60.91	60.15

Several attempts were made to get a better yield of ester by using 2 or 3 molecular proportions of potassium hydroxide and an excess of ethyl iodide, but the results were poorer than when the above proportions were used. The portion that did not esterify was identified as the unaltered acid and was used again to obtain more of the ester.

2-Amino-4,5-diiodbenzoic acid did not esterify to any marked extent with alcohol and sulphuric acid after heating for 5 hours. A small quantity of ester was obtained by dissolving 0.5 gram of the acid in alcohol and passing a stream of hydrogen chloride through the hot solution for an hour. It was identical with the product obtained by alkylating the potassium salt with ethyl iodide.

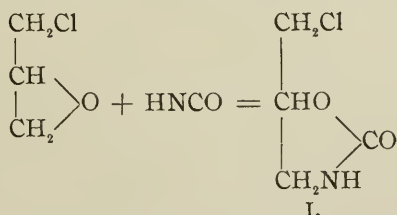
[Contributions from the Sheffield Laboratory of Yale University.]

CLXXXV.—STUDIES IN THE OXAZOLE SERIES:  
THE ADDITION OF CYANIC ACID TO EPICHLOR-  
HYDRIN.

[SECOND PAPER.]

BY TREAT B. JOHNSON AND HERBERT H. GUEST.

In 1878, A. L. Thomsen<sup>1</sup> investigated the behavior of silver and potassium cyanates towards epichlorhydrin. He observed that the silver salt had no action on this chloride, but that potassium cyanate reacted smoothly in aqueous solution, giving a crystalline substance,  $C_4H_6O_2NCl$ . He showed that this reacted with acetic anhydride, giving a monacetyl derivative, and also states that it underwent decomposition when warmed with a dilute solution of potassium hydroxide, giving potassium chloride, potassium carbonate and ammonia. When heated with concentrated hydrochloric acid at  $150^\circ$  carbon dioxide and ammonium chloride were formed and also, to quote from the original, "eine wenig einladende Substanz welche nicht in einem für die Analyse geeigneten Zustande erhalten werden konnte." Thomsen explained the formation of this compound by assuming a simple addition of cyanic acid to epichlorhydrin, and assigned to it, without further proof, the structure of a *ketotetrahydrooxazole* (I). The object of the work described in this paper was to



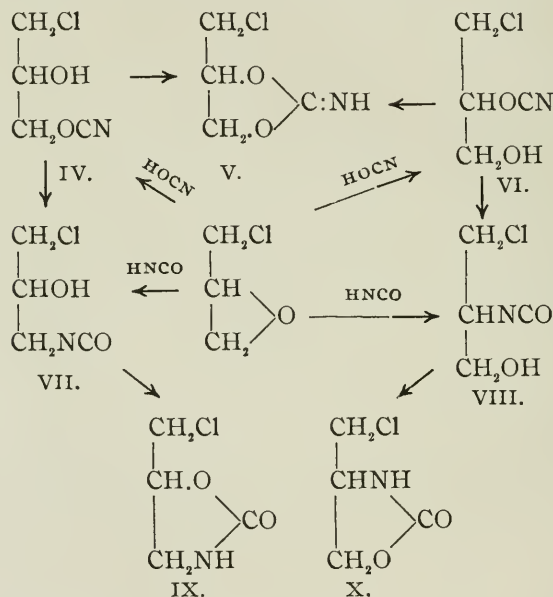
synthesize Thomsen's compound by a new method and therefore determine the manner of addition of cyanic acid to epichlorhydrin.

If we assume that cyanic acid can exist in two tautomeric forms, (II) and (III), and that it behaves in a dilute, aqueous

<sup>1</sup> Ber. d. chem. Ges., 11, 2136.



solution as an electrolyte like hydrochloric acid, several unstable, intermediate products might be formed by its action on epichlorhydrin, according as it undergoes dissociation into H and NCO or H and OCN ions. It could add, theoretically, to this oxide in four ways, giving the unstable, acyclic cyanic and isocyanic esters (IV), (VI), (VII) and (VIII), which



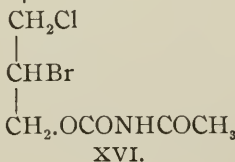
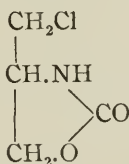
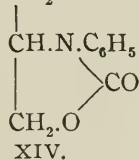
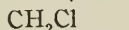
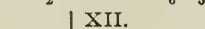
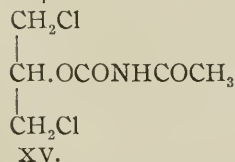
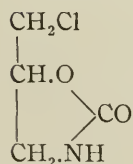
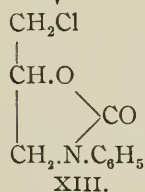
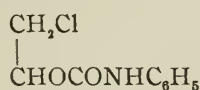
would then undergo rearrangements into the two isomeric ketotetrahydrooxazoles (IX) and (X). The cyanic esters (IV) and (VI), instead of rearranging to the isocyanates (VII) and (VIII), respectively, might also undergo metameric changes, giving the same imidocarbonate (V). Therefore three isomeric, cyclic compounds might theoretically be formed by the action of cyanic acid on epichlorhydrin, *viz.*,  $\beta$ -chlormethyl- $\mu$ -ketotetrahydrooxazole (IX),<sup>1</sup>  $\alpha$ -chlormethyl-

<sup>1</sup> The writer desires to correct here a typographical error in the first paper of this series (THIS JOURNAL, 44, 352). The ketotetrahydrooxazoles should be designated as  $\mu$ -keto instead of  $\omega$ -keto derivatives.



$\mu$ -ketotetrahydrooxazole (X), and  $\alpha$ -chlorpropyleneglyceryl imidocarbonate (V).

In a previous paper from this laboratory Johnson and Langley<sup>1</sup> have described the phenylurethanes of all the haloid esters of glycerol containing chlorine and bromine. They observed that these compounds are especially characterized by their behavior in the presence of alkali, and undergo transformations into ketotetrahydrooxazoles with loss of a halogen acid. For example:  $\beta,\beta'$ -dichlorisopropyl phenylcarbamate (XI) and  $\beta$ -brom- $\gamma$ -chlorpropyl phenylcarbamate (XII) were converted into the *N*-phenyl derivatives of  $\beta$ -chlor-methyl- $\mu$ -ketotetrahydrooxazole (IX) and  $\alpha$ -chlormethyl- $\mu$ -



<sup>1</sup> THIS JOURNAL, 44, 352.

ketotetrahydrooxazole (X), or  $\beta$ -chlormethyl-N-phenyl- $\mu$ -keto-tetrahydrooxazole (XIII) and  $\alpha$ -chlormethyl-N-phenyl- $\mu$ -keto-tetrahydrooxazole (XIV), respectively, when warmed with a strong solution of potassium hydroxide. It might be expected, therefore, that the corresponding acylurethanes (XV) and (XVI) would undergo analogous changes, in the presence of alkali, giving the corresponding tetrahydrooxazoles (IX) and (X), with formation of an aliphatic acid by hydrolysis. The acetyl- and benzoylurethanes of the haloid esters of glycerol were easily obtained by the action of acetyl- and benzoyl isocyanates<sup>1</sup> on these alcohols. These acyl cyanates, which have been little investigated, are far more reactive than phenyl isocyanate and the corresponding urethanes were all well-characterized, crystalline compounds. The benzoyl derivatives are more suitable for the identification of these glycerol haloid esters than the acetyl- or phenylurethanes because of their lesser solubility in the common organic solvents and their more characteristic melting points.

We now find that  $\beta,\beta'$ -dichlorisopropyl acetylcarbamate (XV) and the corresponding benzoylurethane are both changed, by the action of strong alkali, into a cyclic compound which is identical with the substance  $C_4H_6O_2NCl$  obtained by Thomsen<sup>2</sup> by treatment of epichlorhydrin with potassium cyanate. Furthermore, these two acylurethanes condense like the phenylurethane examined by Johnson and Langley, and the cyclic compound is therefore assigned the structure of  $\alpha$ -chlormethylketotetrahydrooxazole, as originally represented by Thomsen.<sup>3</sup> That it has not the structure of  $\alpha$ -chlorpropyleneglyceryl imidocarbonate (V) is established by the following facts: It is soluble in alkali without decomposition, indicating the presence of a CO.NH grouping, and gives a monosilver salt. The compound apparently possesses no basic properties. A cyclic compound having the structure of an imidocarbonate (V) would be expected to possess properties similar to those of an acyclic imidocarbon-

<sup>1</sup> Billeter: Ber. d. chem. Ges., **36**, 3213.

<sup>2</sup> Loc. cit.

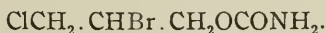
<sup>3</sup> Loc. cit.

ate, diethyl imidocarbonate,  $\text{HN}:\text{C}(\text{OC}_2\text{H}_5)_2$ ,<sup>1</sup> and undergo hydrolysis, giving ammonia. Thomsen states that his compound underwent decomposition, with evolution of ammonia, when digested with dilute alkali. We are not able to confirm this statement, and obtained no evidence of the formation of any ammonia by digestion with an excess of a 20 per cent. solution of sodium hydroxide. It seems very probable to the writer that the ammonia detected by Thomsen resulted from a decomposition of a cyanate or some urea(?), which accompanied his tetrahydrooxazole as impurities.

The fact that  $\beta,\beta'$ -dichlorisopropyl acetyl- and benzoyl-carbamates are converted into the same tetrahydrooxazole (IX) as is obtained by the action of potassium cyanate, in aqueous solution, on epichlorhydrin, shows that cyanic acid adds to this oxide in an analogous manner to the halogen acids, giving a secondary alcohol. *Therefore the NCO radical attaches itself to the carbon atom 3 at the end of the chain*

$\overset{1}{\text{—C}}.\overset{2}{\text{C}}.\overset{3}{\text{C—}}$ . Whether this involves primarily an addition of H- and -OCN ions, giving a cyanic ester, and a subsequent rearrangement to an isocyanate, we have no evidence.

Attempts to prepare the isomeric  $\alpha$ -chlormethyl- $\mu$ -keto-tetrahydrooxazole (X) by the action of alkali on  $\beta,\gamma$ -dichloropropyl and  $\beta$ -brom- $\gamma$ -chlorpropyl acetylcarbamates were unsuccessful. The former urethane dissolved in cold alkali, without decomposition, giving a crystalline sodium salt, while the latter underwent hydrolysis under the same conditions, giving the urethane of  $\beta$ -brom- $\gamma$ -chlorpropyl alcohol,



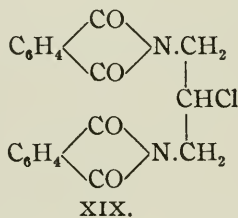
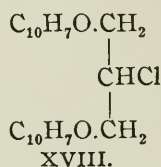
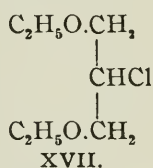
When heated with alkali, both urethanes underwent decomposition with formation of ammonia. In the case of the corresponding phenylurethanes<sup>2</sup> it was possible to change both forms into their corresponding oxazoles. However, it was observed that there was a remarkable difference in the ease with which these changes could be effected. The phenylurethanes of the  $\alpha$ -dihalohydrins underwent the transformation

<sup>1</sup> Sandmeyer: Ber. d. chem. Ges., **19**, 864. Nef: Ann. Chem. (Liebig), **287**, 285. Hantzsch and Mai: Ber. d. chem. Ges., **28**, 2470.

<sup>2</sup> Johnson and Langley: *Loc. cit.*

practically quantitatively at  $50^{\circ}$ – $60^{\circ}$ , while, on the other hand, the corresponding urethanes of the  $\beta$ -dihalohydrins ( $\beta$ -dichlorhydrin) showed lesser tendency to undergo cyclization under these conditions and were partly decomposed.

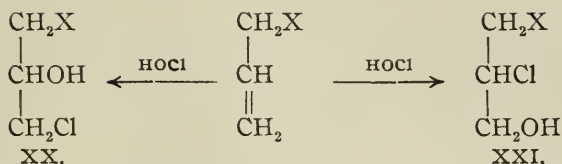
These results again illustrate, in a striking manner, the remarkable stability of secondary halides of the general formula  $XCH_2CHCl.CH_2X$ . Reboul and Lourenco,<sup>1</sup> who examined the action of sodium ethylate on  $\alpha,\gamma$ -diethoxy- $\beta$ -chlorpropane (XVII), write: "Durch eine concentrirte Lösung von Natriumalkoholat wird sie angegriffen, doch muss man zu Vervollständigung der Einwirkung das Gemische in einer zugeschmolzenen Rohre während einiger Stunden auf  $120^{\circ}$  erhitzen." The writer has also recently observed that  $\alpha,\gamma$ -di- $\beta$ -naphthoxy- $\beta$ -chlorpropane (XVIII) and  $\alpha,\gamma$ -diphthalimido- $\beta$ -chlorpropane (XIX) can be digested with sodium ethylate for hours without removal of the halogen atom.



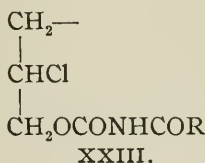
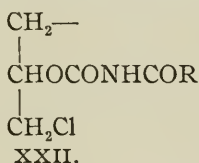
A simple method of determining easily the manner of addition of hypochlorous acid to allyl compounds is lacking. The common method is to subject the chlor alcohols obtained to oxidation<sup>2</sup> and ascertain by examination of the products of oxidation whether the original halohydrin was a secondary (XX) or a primary alcohol (XXI). In some cases, however,

<sup>1</sup> Ann. Chem. (Liebig), **119**, 238; Spl., **1**, 237.

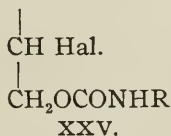
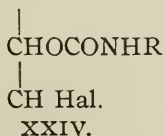
<sup>2</sup> Ber. d. chem. Ges., **40**, 94.



the hypochlorous acid adds in both ways, giving a mixture of alcohols which it is difficult to separate. The oxidation reactions also are oftentimes not smooth and consequently the products of the reaction are not formed in sufficient amount to purify and permit of identification with accuracy. Our observation of the remarkable difference in behavior, towards cold alkali, of acylurethanes of the types (XXII) and (XXIII) is therefore of especial interest.



It is the intention of the writer to continue the study of urethanes of the general formulas (XXIV) and (XXV):



#### EXPERIMENTAL PART.

*β,β'-Dichlorisopropyl Acetylcarbamate*,  
 $\begin{array}{c} \text{CH}_2\text{Cl} \\ | \\ \text{CHOCONHCOCH}_3 \end{array}$ —Twelve grams of acetyl isocyanate, dissolved in dry ether, were added slowly to a cold ether solution of 18 grams of  $\alpha$ -dichlorhydrin. There was an immediate reaction, with evolution of much heat, and in a few minutes a crystalline magma of the urethane was obtained. The yield was 28 grams, corresponding to 93 per cent. of the theo-

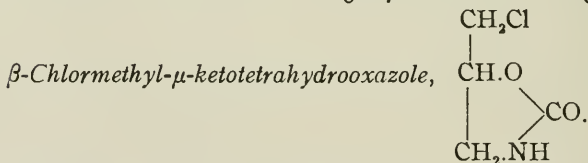
retical. It is soluble in benzene, hot water and alcohol. It was purified for analysis by crystallization from 95 per cent. alcohol and separated in clusters of needles melting at  $100^{\circ}$  to an oil. Analysis (Kjeldahl):

	Calculated for $C_6H_9O_3NCl_2$ .	Found.
N	6.54	6.47

$\beta, \beta'$ -Dichlorisopropyl Benzoylcarbamate,  
 $\begin{array}{c} CH_2Cl \\ | \\ CHOCONHCOC_6H_5 \end{array}$

—This urethane was prepared like the preceding acetylcarbamate by the addition of 16 grams of benzoyl isocyanate to 16 grams of  $\alpha$ -dichlorhydrin. It separated from the ether in colorless prisms which were purified by crystallization from alcohol. It crystallized in rectangular prisms which melted sharply at  $119^{\circ}$  to an oil. The compound is very soluble in benzene and insoluble in water. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NCl_2$ .	Found.
N	5.07	5.02



*Preparation from  $\beta, \beta'$ -Dichlorisopropyl Acetylcarbamate.*—Ten grams of potassium hydroxide were dissolved in 20 cc. of water and 5 grams of the acetylcarbamate added in portions to the alkali solution. The urethane dissolved at once, with evolution of heat, and the solution gave a strong test for the chlorine ion. The excess of alkali was then neutralized with hydrochloric acid and the solution evaporated to dryness. The residue obtained was extracted with alcohol to remove the greater part of the potassium chloride and when the alcohol was evaporated we obtained the crude ketotetrahydrooxazole in crystalline form. It was purified by recrystallization from hot water and finally benzene. It separated from the lat-



ter solvent in prismatic crystals, which melted at  $105^{\circ}$ – $106^{\circ}$  to a clear oil. A mixture of this substance and of Thomsen's<sup>1</sup> compound (melting at  $106^{\circ}$ ) melted at exactly the same temperature.

In a second experiment 5 grams of potassium hydroxide were dissolved in 20 cc. of water and 5 grams of the urethane added slowly to the solution as before. This dissolved immediately, and after allowing to stand for about 10 minutes, the alkaline solution was neutralized (cold) with hydrochloric acid. On standing, the oxazole separated in colorless prisms and after one crystallization from water melted at  $106^{\circ}$ . More of the compound was obtained from the filtrate in the manner described in the first experiment. Analysis:

	Calculated for $C_4H_6O_2NCl$ .	Found.
Cl	26.63	26.30

*Preparation from  $\beta,\beta'$ -Dichlorisopropyl Benzoylcarbamate.*—Three-tenths gram of sodium was dissolved in absolute alcohol and 3.0 grams of the carbamate added at once to the solution. There was an immediate reaction, with separation of sodium chloride, and with evolution of sufficient heat to cause the solution to boil. After heating about 10–15 minutes, on the steam bath, the sodium chloride was filtered off and the alcohol filtrate concentrated. We obtained an oil which was insoluble in cold water and having a strong odor of ethyl benzoate. It was dissolved in ether to remove inorganic salts and when the solution was allowed to evaporate spontaneously we obtained a crop of prisms suspended in ethyl benzoate. They melted at  $105^{\circ}$ – $106^{\circ}$ , without further purification, and were identified as  $\beta$ -chlormethyl- $\mu$ -ketotetrahydro-oxazole. When the oil was digested with alkali it dissolved, and on addition of hydrochloric acid to the alkaline solution benzoic acid melting at  $120^{\circ}$  separated. The yield of oxazole obtained from the benzoylcarbamate was small. Analysis (Kjeldahl):

	Calculated for $C_4H_6O_2NCl$ .	Found.
N	10.3	10.0

<sup>1</sup> Loc. cit.

*Digestion of  $\beta$ -Chlormethylketotetrahydrooxazole with Alkali.*—About 0.1 gram of the oxazole was dissolved in 350 cc. of 20 per cent. sodium hydroxide and the solution subjected to a Kjeldahl distillation, the distillate being passed into 10 cc. of 0.1 N hydrochloric acid. After distilling over about one-half the liquid, 9.85 cc. of a 0.1 N sodium hydroxide solution, were required to neutralize the free hydrochloric acid present.

*Silver Salt of  $\beta$ -Chlormethylketotetrahydrooxazole.*—This separated as a white, gelatinous precipitate when the calculated quantity of silver nitrate was added to an aqueous solution of the sodium salt of the ketotetrahydrooxazole. After washing with water and alcohol it was dried for analysis in a desiccator over concentrated sulphuric acid.

	Calculated for $C_4H_5O_2NClAg$ .	Found.
A	44.54	46.0

*$\beta$ -Chlormethylketotetrahydrooxazylphenylurea,*

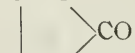


—This urea was prepared by warming at 100°  $\beta$ -chlormethylketotetrahydroxazole, prepared by our method and also by Thomsen's, with a molecular proportion of phenyl isocyanate. It crystallized from alcohol in rhombic tables melting at 154°–155° to an oil without effervescence. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3N_2Cl$ .	Found.
N	11.00	10.60

$\beta$ -Chlormethylketotetrahydrooxazole was recovered unaltered after heating with phenyl isothiocyanate at 100° for 3 days.

*$\beta$ -Chlormethylketotetrahydrooxazylbenzoylurea,*



—A quantitative yield of this urea was

obtained by warming 0.8 gram of the tetrahydrooxazole with 0.9 gram of benzoyl isocyanate for a few minutes at  $100^{\circ}$ . It crystallizes from 95 per cent. alcohol in rhombic prisms, which melt at  $131^{\circ}$ – $132^{\circ}$  to an oil. Analysis (Kjeldahl):

	Calculated for $C_{12}H_{11}O_4N_2Cl$ .	Found.
N	9.9	9.55

*$\beta,\gamma$ -Dichloropropyl Acetylcarbamate,*

$CH_2Cl$

|

$CHCl$

|

$CH_2OCONHCOCH_3$ .—Acetyl isocyanate reacts immediately with  $\beta,\gamma$ -dichloropropyl alcohol in ether, giving a quantitative yield of this urethane. When the ether was allowed to evaporate spontaneously it deposited in colorless prisms which were very soluble in benzene, alcohol and acetone, but insoluble in ligroin. It was purified by crystallization from benzene and separated in well-developed prisms melting at  $64^{\circ}$ – $65^{\circ}$  to an oil. Analysis (Kjeldahl):

	Calculated for $C_6H_9O_3NCl_2$ .	Found.
N	6.55	6.60

*Action of Alkali on  $\beta,\gamma$ -Dichloropropyl Acetylcarbamate.*—Three and five-tenths grams of this urethane were added to 15 cc. of a cold aqueous solution of potash, prepared by dissolving 1 part of the alkali in 4 parts of water. It dissolved at once and then suddenly a sodium salt separated in the form of glistening plates. These were filtered off and dissolved in water and hydrochloric acid added cautiously to the solution when an oil separated which soon crystallized. The substance was very soluble in alcohol, benzene, and insoluble in ligroin. After purification by crystallization from benzene it melted at  $64^{\circ}$ – $65^{\circ}$  and was identified as the unaltered  $\beta,\gamma$ -dichloropropyl acetylcarbamate. Analysis (Kjeldahl):

	Calculated for $C_6H_9O_3NCl_2$ .	Found.
N	6.55	6.50

*Allyl Acetylcarbamate,*  $CH_2:CH.CH_2O.CO.NHCOCH_3$ .—

This was prepared by the action of acetyl isocyanate on allyl alcohol in ether solution. It is very soluble in benzene, ethyl alcohol and chloroform. It was purified by crystallization from a mixture of benzene and ligroin and separated in long, flat prisms melting at  $64^{\circ}$  to an oil. *Analysis* (Kjeldahl):

	Calculated for $C_6H_9O_3N$ .	Found.
N	9.86	9.80

*$\beta$ -Brom- $\gamma$ -chlorpropyl Acetylcarbamate,*



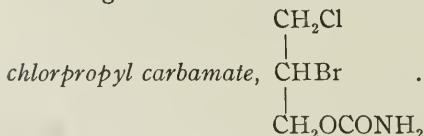
—Four grams of  $\beta$ -brom- $\gamma$ -chlorpropyl alco-

hol and 2 grams of acetyl isocyanate were dissolved in ether and the solution allowed to evaporate spontaneously. The urethane separated as an oil. This finally solidified on standing and was purified for analysis by dissolving in benzene and precipitating from this solvent with ligroin. It separated as an oil, which soon crystallized in prisms, melting at  $60^{\circ}$  to an oil. The urethane is very soluble in alcohol and benzene. *Analysis* (Kjeldahl):

	Calculated for $C_6H_9O_3N\text{ClBr}$ .	Found.
N	5.34	5.42

*Action of Alkali on  $\beta$ -Brom- $\gamma$ -chlorpropyl Acetylcarbamate.*—

Eight grams of potassium hydroxide were dissolved in 32 cc. of water and 8 grams of the carbamate added to the cold solution. It dissolved immediately on stirring and in a few minutes a colorless crystalline substance separated. This was insoluble in cold water and very soluble in alcohol, but crystallized from dilute alcohol in plates melting at  $93^{\circ}$ . The compound contained chlorine and bromine and when warmed with alkali, it was decomposed with evolution of ammonia. A nitrogen determination indicated that it was  $\beta$ -brom- $\gamma$ -



	Calculated for $C_4H_7O_2NClBr$ .	Found.
N	6.47	6.32

The following urethanes were all prepared by dissolving the corresponding alcohols in ether and then adding the calculated quantity of benzoyl isocyanate diluted with ether. In some cases the urethanes separated in crystalline form in a short time, but in others they were very soluble and were obtained, after spontaneous evaporation of the ether, as oils which soon crystallized on standing.

*$\beta,\beta'$ -Dibromisopropyl Benzoylcarbamate,*

$(BrCH_2)_2CHOCONHCOC_6H_5$ .—From  $\alpha$ -dibromhydrin and benzoyl isocyanate. It is very soluble in benzene and crystallizes from alcohol in plates melting at  $119^\circ$ . Analysis (Kjeldahl):

	Calculated for $C_1 H_{11}O_3NBr_2$ .	Found.
N	3.84	3.83

*$\beta,\beta'$ -Chlorbromisopropyl Benzoylcarbamate,*

$CH_2Br$   
|  
 $CHOCONHCOC_6H_5$ .—From  $\alpha$ -chlorbromhydrin and benzoyl  
|  
 $CH_2Cl$   
isocyanate. It separated from the ether in colorless crystals and crystallized from alcohol in long needles melting at  $122^\circ$ . Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NClBr$ .	Found.
N	4.37	4.18

*$\beta,\gamma$ -Dichloropropyl Benzoylcarbamate,*

$ClCH_2.CHCl.CH_2OCONHCOC_6H_5$ .—This was obtained as an oil, after evaporation of the ether, which finally crystallized on standing. It is very soluble in alcohol, benzene and acetone. It was purified by crystallization from a mixture of benzene and ligroin and melted at  $83^\circ$ . Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NCl_2$ .	Found.
N	5.07	5.30

 *$\beta,\gamma$ -Dibromopropyl Benzoylcarbamate,*

$BrCH_2CHBr.CH_2OCONHCOC_6H_5$ .—This urethane is very soluble in alcohol, ether and benzene. It was purified by crystallization from a mixture of benzene and ligroin and melted at  $83^\circ$  to an oil. Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NBr_2$ .	Found.
N	3.83	3.78

 *$\beta$ -Brom- $\gamma$ -chlorpropyl Benzoylcarbamate,*

$ClCH_2CHBr.CH_2OCONHCOC_6H_5$ .—This is very soluble in ether, benzene and alcohol. It crystallized from cold ethyl and methyl alcohols in tabular crystals melting at  $113^\circ$ . A mixture of this compound and of  $\beta,\beta'$ -chlorbromisopropyl benzoylcarbamate (melting at  $122^\circ$ ) melted at  $110^\circ$ – $115^\circ$ . Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NClBr$ .	Found.
N	4.37	4.25

 *$\beta$ -Chlor- $\gamma$ -brompropyl Benzoylcarbamate,*

$BrCH_2CHCl.CH_2OCONHCOC_6H_5$ .—This urethane was obtained as an oil which crystallized on long standing. It is very soluble in all the common organic solvents except ligroin. It was purified by crystallization from alcohol and separated in prisms melting at  $114^\circ$ . A mixture of this urethane and of  $\beta,\beta'$ -dichlorisopropyl benzoylcarbamate melted at  $110^\circ$ – $116^\circ$ . A mixture of the urethane and of the isomeric  $\beta$ -brom- $\gamma$ -chlorpropyl benzoylcarbamate melted at  $113^\circ$ – $114^\circ$ . Analysis (Kjeldahl):

	Calculated for $C_{11}H_{11}O_3NClBr$ .	Found.
N	4.37	4.50

NEW HAVEN, CONN.,  
June 15, 1910.



# THE PRECIPITATION OF VANADIC ACID AS SILVER VANADATE, AND THE ESTIMATION OF PHOSPHORIC AND VANADIC ACIDS IN THE PRESENCE OF ONE ANOTHER.

BY GRAHAM EDGAR.

## *I. The Precipitation of Vanadic Acid as Silver Vanadate.*

Three salts of silver and vanadic acid have been described by Ditte<sup>1</sup> and others, the dark red orthovanadate,  $\text{Ag}_3\text{VO}_4$ , the dark yellow crystalline pyrovanadate,  $\text{Ag}_4\text{V}_2\text{O}_7$ , and the pale yellow metavanadate,  $\text{AgVO}_3$ . All of these are insoluble in water and dilute acetic acid, and soluble in ammonium hydroxide and nitric acid. They may be readily obtained by the action of silver nitrate upon fresh solutions of the corresponding alkali salts, but unless special precautions are taken mixtures of the various salts are always formed. The writer has thought it desirable to study the character of the precipitate formed by silver nitrate and solutions of alkali vanadate under various conditions, with the object of finding conditions under which a precipitate of constant composition is formed, thus permitting the quantitative estimation of vanadic acid as silver salt, either gravimetrically, or volumetrically by an adaptation of the well-known Volhard method for the estimation of silver.

In all of the experiments described below the same general plan was followed; a known quantity of standard solution of sodium vanadate was treated with an excess of 0.1 N silver nitrate, and the excess of silver was determined in the filtrate from the precipitated silver vanadate by titration with standard ammonium thiocyanate. The composition of the precipitate was then calculated from the amount of silver used, qualitative tests having shown that the filtrate contained no vanadium.

In Table (Ia) are given the results of experiments made on a solution of pure sodium pyrovanadate. The method of treatment was as follows: To measured portions of the solu-

<sup>1</sup> Compt. rend., 104, 1705.

tion a considerable excess of 0.1 N silver nitrate was added, the precipitate was dissolved in the least possible quantity of ammonium hydroxide, and the solution was boiled until the odor of ammonia had disappeared. The flask was then cooled and allowed to stand for a few minutes. Under these conditions a dark red precipitate was obtained which settled readily, leaving a colorless solution. The solution was filtered through asbestos on a perforated crucible, and the filtrate was titrated with ammonium thiocyanate, after the addition of nitric acid and ferric nitrate. The results show that under these conditions the vanadic acid is quantitatively precipitated as silver orthovanadate,  $\text{Ag}_3\text{VO}_4$ , and that in a solution of pure sodium pyrovanadate, the vanadium may be very simply estimated in this manner:

Table Ia.

$\text{V}_2\text{O}_5$ taken. Gram.	0.1 N $\text{AgNO}_3$ required. cc.	$\text{V}_2\text{O}_5$ found. Gram.	Error $\text{V}_2\text{O}_5$ . Gram.	Remarks.
0.1183	38.94	0.1184	+0.0001	Calculated as $\text{Ag}_3\text{VO}_4$
0.1183	38.88	0.1182	—0.0001	
0.0503	16.58	0.0504	+0.0001	
0.0887	29.18	0.0887	$\pm 0.0000$	
0.0887	29.18	0.0887	$\pm 0.0000$	
0.0591	19.37	0.0589	—0.0002	
0.0591	19.44	0.0591	$\pm 0.0000$	

Table Ib.

0.0887	19.41	0.0885	—0.0002	Calculated as $\text{Ag}_4\text{V}_2\text{O}_7$ Acidified with acetic acid
0.0887	19.39	0.0884	—0.0003	
0.0887	19.39	0.0884	—0.0003	
0.0591	12.89	0.0587	—0.0004	
0.0591	12.90	0.0588	—0.0003	Acidified with nitric acid
0.0591	12.95	0.0590	—0.0001	
0.0887	19.41	0.0885	—0.0002	
0.0887	19.41	0.0885	—0.0002	

In Table Ib are given the results of experiments in which the solution of sodium pyrovanadate was acidified with acetic or nitric acid, before the addition of the silver nitrate. Ammonium hydroxide was then added, and the determinations carried out as before. The results show that under these

conditions the pyrovanadate,  $\text{Ag}_4\text{V}_2\text{O}_7$ , is precipitated, the results being nearly quantitative, though a little low in every case. In this process, however, great difficulty was experienced in preventing the violent bumping of the solution during the boiling off of the ammonia, fragments of porous tile being entirely inadequate to prevent this.

Either of the above methods would give satisfactory results for the estimation of vanadium in a solution of pure sodium vanadate, but it is obvious that to be of practical use a method must be applicable to the solutions of vanadium obtained in the ordinary course of analysis, which usually are either acid or else contain an indefinite amount of alkali. Accordingly a solution of sodium vanadate was prepared by boiling barium vanadate with an excess of sodium carbonate, and filtering from the barium carbonate. This solution was used in all the work described below.

Experiments showed that if such a solution is acidified with nitric acid, boiled to expel the carbon dioxide, and then neutralized with calcium carbonate, direct precipitation with silver nitrate gives a precipitate of varying composition, consisting largely of the pyrovanadate. If this precipitate is dissolved in ammonium hydroxide and reprecipitated by boiling off the ammonia, the orthovanadate is formed, but the calcium carbonate reacts to some extent with the silver nitrate, causing uncertain results.

The plan was then tried of acidifying the vanadate solution with nitric acid, boiling off the carbon dioxide as before, and then adding dilute sodium hydroxide to the boiling solution until the yellow color had disappeared. Under these conditions the solution is only faintly alkaline to phenolphthalein, and direct precipitation with silver nitrate gives the metavanadate,  $\text{AgVO}_3$ , the composition of the precipitate, however, varying considerably. If ammonium hydroxide is added and the excess of ammonia removed by boiling, the orthovanadate,  $\text{Ag}_3\text{VO}_4$ , is precipitated, and excellent results may be obtained for the estimation of vanadium. Table II gives some results obtained in this manner. The following directions may, therefore, be given for the estimation of vana-

Table II.

$V_2O_5$ taken. Gram.	0.1 N $AgNO_3$ . cc.	$V_2O_5$ found. Gram.	Error. Gram.
0.1257	41.32	0.1256	—0.0001
0.1257	41.40	0.1258	+0.0001
0.1257	41.35	0.1257	±0.0000
0.0628	20.60	0.0626	—0.0002
0.0628	20.66	0.0628	±0.0000
0.1885	62.00	0.1885	±0.0000
0.1885	62.04	0.1886	+0.0001
0.1257	41.33	0.1256	—0.0001

dium in solutions of alkali vanadate containing an excess of carbonate but no other substance precipitated by silver nitrate in neutral or ammoniacal solution:

The solution is acidified with nitric acid and boiled to expel the carbon dioxide. A yellow color, at first deep and then fading somewhat, is formed by this treatment. Dilute sodium hydroxide is then added to the boiling solution until the color changes back through deep yellow to colorless. An excess of standard silver nitrate solution is then added, the precipitate is dissolved in ammonium hydroxide, and the solution boiled until the odor of ammonia has disappeared. A few fragments of porous tile are added to prevent bumping. The solution is cooled and filtered through asbestos (or paper) and the filtrate is acidified with nitric acid and titrated with standard ammonium thiocyanate. The vanadic acid is calculated on the assumption that the precipitate is the orthovanadate,  $Ag_3VO_4$  (one cc. of 0.1 N  $AgNO_3$  is equivalent to 0.00304 gram of  $V_2O_5$ ). An advantage of this method lies in the smallness of this factor, it being only one-third of that for 0.1 N solutions in the oxidimetric process.

## II. The Estimation of Phosphoric and Vanadic Acids in the Presence of One Another.

Many methods for the separation of phosphoric and vanadic acids have been devised, but none of them are altogether satisfactory. Perhaps the best is that of Holverscheit,<sup>1</sup> in

<sup>1</sup> Diss., Berlin, 1890.

which the phosphoric acid is precipitated by molybdic solution after the reduction of the vanadic acid with sulphur dioxide. This method is accurate, but leaves the vanadium in an unsatisfactory condition for further work.

The use of combined volumetric processes for the estimation of vanadium and other elements in the presence of one another has proved so successful in other instances<sup>1</sup> that it has seemed to the writer that in this case also the separation of phosphoric and vanadic acids might be avoided, and the two estimated in the same solution by precipitation as silver salts. Silver nitrate gives with neutral or slightly alkaline solutions of sodium phosphate a precipitate of yellow silver phosphate,  $\text{Ag}_3\text{PO}_4$ , and if this precipitate is dissolved in ammonium hydroxide, and the excess of ammonia removed by boiling, the phosphoric acid may be estimated volumetrically by the titration of the excess of silver nitrate in the filtrate from the silver phosphate. It is obvious that if vanadic and phosphoric acids were present in the same solution this process would determine the sum of both acids, and if the vanadium were estimated in the precipitate, the phosphoric acid could be determined by difference. Table III gives the results of experiments on solutions containing sodium phosphate and vanadate in varying amounts, together with an excess of sodium carbonate. The technique was exactly the same as that given above for the estimation of vanadium, with the exception that the precipitate of silver vanadate and phosphate was washed back from the filter into the flask in which precipitation was made, and the vanadium was determined by solution in sulphuric acid, reduction with sulphur dioxide, and titration of the hot solution with 0.05 N potassium permanganate, after removing the excess of sulphur dioxide by boiling, a current of carbon dioxide being passed through the solution. The phosphoric acid was then determined by difference (one cc. of 0.05 N  $\text{KMnO}_4$  is equivalent to 0.00456 gram of  $\text{V}_2\text{O}_5$ , and one cc. of 0.1 N  $\text{AgNO}_3$  to 0.00304 gram  $\text{V}_2\text{O}_5$  or 0.0023667 gram of  $\text{P}_2\text{O}_5$ ).

<sup>1</sup> Am. J. Sci., 25, 332; 26, 79, 333; 27, 174, 299. J. Ind. Eng. Chem., 1, 661.



Table III.

V <sub>2</sub> O <sub>5</sub> taken. Gram.	P <sub>2</sub> O <sub>5</sub> taken. Gram.	0.1 N AgNO <sub>3</sub> required. cc.	0.05 N KMnO <sub>4</sub> required. cc.	V <sub>2</sub> O <sub>5</sub> found. Gram.	Error V <sub>2</sub> O <sub>5</sub> . Gram.	P <sub>2</sub> O <sub>5</sub> found. Gram.	Error P <sub>2</sub> O <sub>5</sub> . Gram.
0.1257	0.0331	55.31	27.70	0.1258	-0.0001	0.0329	-0.0002
0.1257	0.0331	55.26	27.68	0.1257	±0.0000	0.0329	-0.0002
0.1257	0.0662	69.26	27.64	0.1255	-0.0002	0.0662	±0.0000
0.0628	0.0662	48.56	13.82	0.0627	+0.0001	0.0661	-0.0001
0.0628	0.0662	48.55	13.84	0.0628	±0.0000	0.0660	-0.0002
0.0628	0.0996	62.50	13.84	0.0628	±0.0000	0.0995	-0.0001
0.1257	0.0996	83.26	27.70	0.1258	+0.0001	0.0994	-0.0002
0.1885	0.0331	75.92	41.50	0.1884	-0.0001	0.0330	-0.0001
0.1885	0.0331	75.95	41.58	0.1888	+0.0003	0.0328	-0.0003
....	0.0331	13.95	....	....	....	0.0330	-0.0001
....	0.0662	27.85	....	....	....	0.0659	-0.0003
....	0.0996	41.92	....	....	....	0.0995	-0.0001

## SUMMARY.

Conditions have been found under which vanadic acid may be quantitatively precipitated as silver orthovanadate, and a process for the estimation of vanadic acid, based on this fact, has been devised.

Phosphoric and vanadic acids may be estimated volumetrically in the presence of one another by precipitation as silver salts under the conditions described above, the vanadium being determined oxidimetrically in the precipitate, and the phosphoric acid by difference.<sup>1</sup>

UNIVERSITY OF VIRGINIA,  
July, 1910.

## OBITUARIES.

HENRY AUGUSTUS TORREY.

August 29, 1871-March 25, 1910.

Henry Augustus Torrey was a professor by right of birth, as his father was H. A. P. Torrey, professor of philosophy in the University of Vermont, and his maternal grandfather was President Torrey of the same institution. After graduating at Burlington, he took the degree of Doctor of Philosophy in

<sup>1</sup> NOTE.—Since the above work was done a paper by Browning and Palmer has appeared in the *Am. J. Sci.*, Sept., 1910, describing a method by which vanadium may be estimated by precipitation as silver metavanadate, the precipitate being ignited and weighed as AgVO<sub>3</sub>.



Chemistry at Harvard University, and continued his studies for a year in Leipzig and Berlin, returning to teach in the University of Vermont from 1898 to 1903, when he was called to Harvard University, and there he remained as instructor and later assistant professor of organic chemistry till the time of his death.

Of his more important investigations, that on the complex phenols, which are insoluble in alkalies, should undoubtedly come first. In this he showed himself a master of the art of testing working hypotheses by well-conceived experiments, and collected so many observations that a firm basis has been secured for the solution of this difficult problem. Next I should place his discovery and thorough study of iodanil, perhaps because my own unsuccessful attempts to make iodorthoquinones have impressed me with the difficulty of such work; but it may be that the second place should be given to his work on pyromucylacetic ester, which furnished another member of the acetacetic ester family, and led to the discovery of new pyrazolones.

Other interesting researches are his study of the complicated reaction of paranitrosodialkylanilines with ethylene dibromide, and of the isomeric red and white silver salts of tribromphenol. His work on the last subject was restricted to a brief excursion into this field to avoid interference with Hantzsch, but even in this he succeeded in throwing much light on these obscure phenomena. His proof that phenoxinone, or quinhydrone, is entirely dissociated when in solution is perhaps the best but not by any means the only example of his fruitful application of physico-chemical methods to organic work.

Without enumerating the subjects of his other papers, enough has been said to show the high quality of his work. The quantity also is considerable, as his chemical activity will be represented by over twenty-five papers, when all his work has been published. With the exception of very few, these date from his less than seven years of service in Cambridge, where the burden of teaching was lightened enough to allow him time for research; and this large production becomes the more remarkable when it is known that for the last twenty years of his life he was suffering from a disability, under which almost any other man would have sunk into a hopeless invalid; but with him it interfered with no duty, and was borne in such heroic silence that his most intimate colleagues knew nothing of its existence, until after it had killed him.

In addition to his capacity for original work, he possessed exceptional ability as a teacher, which thronged his classes in organic chemistry with eager and enthusiastic students.

The loss of his retiring but most attractive personality brings a keen sorrow to his colleagues and friends, and all chemists must grieve that the Science has been deprived of the brilliant future foretold by what he had already accomplished.

C. LORING JACKSON.

HUGO ERDMANN.

Professor Hugo Erdmann, of Berlin, Germany, who was drowned while yachting on June 25th, was born in East Prussia in 1862, and was therefore 48 years old at the time of his death.

Graduating from the Gymnasium at Tilsit, Erdmann studied in the universities of Halle, Munich and Strassburg. In 1883 he was chosen as assistant to Volhard in the Halle laboratory; in 1885 he became Privat-dozent, and in 1894 professor. In 1901 he was called to Berlin as Professor of Inorganic Chemistry and Director of the Laboratory in the Royal Institute of Technology at Charlottenburg.

His first scientific work was a share in the investigations of his teacher, Fittig, at Strassburg, on the unsaturated acids; in the course of these researches he accomplished the synthesis of  $\alpha$ -naphthol from phenylisocrotonic acid. His work in the earlier years of his stay in Halle was in both inorganic and organic chemistry, and his books, "*Anleitung zur Darstellung chemischer Präparate*" (inorganic), published in 1891, and "*Anleitung zur Darstellung organischer Präparate*," published in 1894, made his name familiar to students.

The publication of the first of these books brought about a change in the laboratory methods of teaching inorganic chemistry. Many teachers in this country, in England and in Germany, use either Erdmann's book or one of its many successors, thus returning from the method of laboratory instruction by analysis only to the use of both analysis and preparations which was the method of Wöhler. We should not forget that Erdmann was the leader of this movement.

Erdmann's "*Lehrbuch der anorganischen Chemie*," published in 1898, met with a reception so favorable that a fourth edition appeared in 1906. This book is his greatest achievement; it stands in a class by itself; it is a descriptive textbook unrivaled and unapproached in its combined accuracy, completeness and compactness.

Collaborating with Köthner, he published, in 1905, a book on the "Constants of Nature."

His later experimental work was mostly in the inorganic field. He was much interested in the gases of the atmosphere and devised an improved apparatus for isolating argon. He gave much time to the study of liquid air and the accurate separation of its constituents; starting from the fact that solid nitrogen melts  $20^{\circ}$  higher than solid oxygen, he devised apparatus in which all of the nitrogen in a vessel of liquid air is frozen while all of the oxygen remains liquid, pure nitrogen and pure oxygen being obtained by filtration. The importance of pure nitrogen in making calcium cyanamide led him to patent this process.

Among his later articles is his work on thiozonides, or organic derivatives of the active form of sulphur  $S_3$ , corresponding to ozone.

Through the death of Erdmann, cut off in the fulness of his activity, inorganic chemistry has lost an energetic and productive worker.

E. R.

CHARLES ANTHONY GOESSMANN.

Charles Anthony Goessmann, Ph.D., LL.D., Honorary Professor of Chemistry in the Massachusetts Agricultural College, and Honorary Director of the Massachusetts Agricultural Experiment Station, died at his home in Amherst, Mass., on September 1, 1910, at the age of 83.

Dr. Goessmann was born in Naumburg-Hesse, Germany, June 13, 1827. He was a student of Wöhler, under whom he took his doctor's degree at Göttingen in 1852, and it was due to this master's influence that he gave up his plan of becoming a pharmacist and took up the work of pure chemistry. He remained at Göttingen until 1857 as Wöhler's assistant, and it was during this time that he met the two Americans who were instrumental in bringing him to this country.

The Eastwick Bros. owned sugar plantations in Cuba and at their request Dr. Goessmann came to Philadelphia in 1857 as chemist and manager of their sugar company. He remained in this position until 1860, when he resigned and spent several months in Cuba, studying the production of sugar cane on the plantations there. In April, 1861, he entered the employ of the Onandaga Salt Co., of Syracuse, N. Y., where he remained until 1869. From 1861-1864 he was Professor of Chemistry and Physics in the Rensselaer Polytechnic Institute. In 1869, at the invitation of another of his Göttingen friends, President W. S. Clark, of the Massachusetts Agricultural College, he accepted the chair of Chemistry in this newly established institution. In either active or honorary service he held this position for a period of 41 years, until his death.

While professor of Chemistry in the college, he held simultaneously the positions of chemist to the Massachusetts State Board of Agriculture and State Inspector of Fertilizers, and analyst to the State Board of Health. In 1882, when the Massachusetts State Experiment Station was established, he became director and chemist, a position which he held until his retirement in 1907. He was a member of various scientific societies and commissions, being president of the American Chemical Society in 1887. He was one of the founders and was first president of the Association of Official Agricultural Chemists. In 1889 Amherst College gave him the degree of LL.D. In 1907 the trustees of the Carnegie Foundation granted him a pension and he retired from active service.

Coming to this country, as he did, just at the time when the idea of agricultural colleges and experiment stations was developing, it was only natural that a chemist, with a taste for the practical applications of his science, should have found inviting opportunities for taking part in the establishment and shaping of such institutions. He took a leading part in the shaping of the policies of our agricultural experiment stations, and this was especially true in connection with the questions of fertilizers and fertilizer control. It was largely through his influence and labor that the first Massachusetts state law for the control of fertilizer manufacture was passed and he naturally became chemist in charge of the inspection and analysis. This was pioneer work in this field, but the ideas and policies he advocated have since been adopted in practically all laws which have to do with fertilizer control.

His own tastes, his work with Wöhler, the inspiration of Liebig's views on the relation of chemistry to agriculture, his brief connection with sugar refining and the sugar plantations of Cuba and his call to the chair of Chemistry in one of the new agricultural colleges, all led him into the agricultural side of his science. His more important contributions to Chemistry, which number about two hundred, are therefore chiefly along the lines of investigations in pure and practical agriculture, such as sugar and sugar cane, soils, plant composition and plant nutrition, fertilizers, animal feeding, etc. His researches on plant composition and plant nutrition and on animal feeding—lines of work for which the experiment station of which he was so long director and chemist, has become so well known—are perhaps his greatest contribution to agricultural chemistry. During his stay at Göttingen, however, he published some twenty-five papers in organic chemistry



on the constituents of Cantharides, The Production of Leucine from Thialdin, The Constitution of Leucine, Arachidic Acid, etc., and while connected with the salt works at Syracuse he visited and investigated the salt deposits in Michigan, Louisiana and Canada, in addition to those of Onandaga Co., N. Y., publishing reports of these investigations.

As Professor of Chemistry in the Massachusetts Agricultural College, Dr. Goessmann was one of those instructors who won the universal esteem of his students. This esteem and the inspiration he gave to all his pupils was founded not only on his gentleness and friendliness as a man, qualities which endeared him to everyone, but also on his integrity and industry as a scientist. His example was that of both the investigator and the teacher. The work he did showed the man he was and his students believed in him and loved him. They saw in him a chemist who was accurate, industrious and practical, a worker who was painstaking and who never hurried, a teacher and man who was friendly and helpful.

On three occasions Professor Goessmann was the recipient of tokens of his students' regard and affection. On his eightieth birthday the Alumni of the Massachusetts Agricultural College presented him with a stained-glass window, symbolic of his life and work, which hangs in the study of his home. At the last Commencement, in June, 1910, the same body presented to their Alma Mater a portrait of their honored teacher, to be hung on the college walls together with those of the other founders of the institution. The last occasion was on October 12th, when the Massachusetts Agricultural College held a memorial service in honor of the man who had recently passed away. At this time Kenyon L. Butterfield, LL.D., President of the institution, Professor Charles Wellington, Dr. Goessmann's successor in the chair of Chemistry in the College, Professor Charles F. Chandler of Columbia University, a fellow student in Göttingen, and President W. E. Stone, of Purdue University, a pupil and coworker, paid loving and honored tribute to the man and the scientist.

JOSEPH H. CHAMBERLAIN.

## REVIEWS.

ABHANDLUNG ÜBER DIE GLYKOLE ODER ZWEIATOMIGE ALKOHOLE UND ÜBER DAS ÄETHYLENOXYD ALS BINDEGLIED ZWISCHEN ORGANISCHER UND MINERALCHEMIE. Von ADOLF WURTZ. OSTWALD'S KLASSIKER DER EXAKTEN WISSENSCHAFTEN, No. 170. Leipzig: Wilhelm Engelmann. 1909. pp. 96. Price, M. 1.80.

These famous articles have been translated and annotated

by M. and A. Ladenburg. The first appeared originally in 1859, the second in 1862. The translators say in regard to them that they belong to the most important by the author, who is one of the greatest chemists of France.

There can be no doubt that these articles strongly influenced the thoughts of chemists and were of great aid in giving clear conceptions of the atomicity of radicals. The difference between the monatomic radical,  $C_2H_5$ , the diatomic radical,  $C_2H_4$ , and the triatomic radical,  $C_3H_5$ , of glycerol, was for the first time brought out, and the recognition of these differences led in turn to the recognition of similar differences between the elements. All this paved the way for the views in regard to constitution put forward a little later by Couper and Kekulé—views that still prevail, although over forty years have elapsed since they were first presented. I. R.

THE OXIDASES AND OTHER OXYGEN CATALYSTS CONCERNED IN BIOLOGICAL OXIDATIONS. By J. H. KASTLE. Hygienic Laboratory, Public Health and Marine Hospital Service of the United States. Bulletin No. 59, December, 1909. Washington: Government Printing Office. 1910. pp. 164.

This bulletin contains an interesting résumé of the literature of the oxidases written by Professor Kastle, who has himself made important contributions to our present knowledge of this intricate subject. The work is divided into three sections. The first contains an excellent account of the historical development of the different theories of oxidation in which the author has incorporated much interesting information of a chemical character not directly connected with the tissue-oxidases. In this way the scope of the essay is advantageously broadened.

The second part is devoted to a more or less detailed account of the oxidizing ferments, while the last section is devoted to the Catalases and Peroxidases.

The work as a whole must be regarded as a very helpful contribution to the literature of a difficult subject. At the same time it appears to the reviewer to be a matter for regret that while many of the less important oxidizing reactions of the tissues are referred to in some detail, the question of the oxidation of the physiologically important substances present in the animal body—especially the amino acids, carbohydrates and fats—is very largely ignored.

A bibliography containing 467 references is a valuable feature.

H. D. DAKIN.



**ALLEN'S COMMERCIAL ORGANIC ANALYSIS.** A Treatise on the Properties, Modes of Assaying, and Proximate Analytical Examination of the Various Organic Chemicals and Products Employed in the Arts, Manufactures, Medicines, etc., with Concise Methods for the Detection and Estimation of their Impurities, Adulterations and Products of Decomposition. Volume I.—Introduction, Alcohols, Yeast, Malt Liquors and Malt, Wines and Spirits, Neutral Alcoholic Derivatives, Sugars, Starch and Its Isomerides, Paper and Paper-making Materials, Vegetable Acids. By the Editors and the Following Contributors: E. F. ARMSTRONG, J. L. BAKER, G. C. JONES, E. SCHLICHTING and R. W. SINDALL. Fourth edition, entirely rewritten. Edited by HENRY LEFFMANN, M.A., M.D., Professor of Chemistry and Toxicology in the Woman's Medical College of Pennsylvania, and in the Wagner Free Institute of Science, Philadelphia, and W. A. DAVIS, B.Sc., A.C.G.I., formerly Lecturer and Assistant in the Chemical Research Laboratory, City and Guilds College, Imperial College of Science and Technology, London. Philadelphia: Blakiston's Son & Co. 1909 pp. x + 576. Price, \$5.00.

Volume I of the fourth edition of Allen's Commercial Organic Analysis has been awaited with interest because of the standard nature of the work and because the field covered is being so rapidly extended; that this edition has followed the last so closely indicates the deserved popularity of the book.

The plan followed in the present volume has been to allot the various subjects treated to specialists; the book has been largely rewritten and has been increased in size to the extent of 20 pages. The chapter on "Alcohols" of previous editions has been divided into "Alcohols," "Malt and Malt Liquors," and "Wines and Potable Spirits." New articles on "Yeast" and "Paper and Paper-making Materials" are included. The scope of the book is therefore considerably broadened.

Inasmuch as it is stated in the preface that "By the selection of contributors from both sides of the Atlantic the work has been made more distinctly international. . . .," it is somewhat surprising that saccharimeters, which are used so extensively in this country, particularly in commercial work, are given but a half-page description.

Cereals other than wheat also receive very scanty treatment; the factor 6.33 is given for the calculation of protein from nitrogen in cereals. The estimation of sugars by means of the refractometer does not mention Geerlig's or other recent work in this field. On page 290, in referring to the solution densities of carbohydrates, it is stated that the "sum of the carbohydrates present in an aqueous solution may be found approximately by allowing an increase of 3.86 in density for each one gram of carbohydrate in 100 cc. of the liquid. This figure is correct for very dilute solutions. . . . ." This figure is recognized as correct only for solutions of an approximate concentration of ten grams per 100 cc.

In the discussion of the determination of volatile acids in wines the Sellier apparatus, as recommended by Hortvet, which appears to be of great value, is not mentioned. The hydrochloric acid-iron test for formaldehyde is stated to produce a "red" color, which would be misleading to one unfamiliar with the color produced.

On page 358 is found the sentence "... in accordance with the provisions of the U. S. (Federal) food law the following *eight* colors are permitted,..." which is apparently a typographical error. "Laeonlose," on page 401, should be *levulose*. On page 497 is the statement that "Cider vinegar is *yellowish*, has an odor of apples, a sp. gr. of 1.013 to 0.115," which obviously is not an accurate description of this product. From "1.5 to 1.8 per cent. of extract" would seem to be a narrow margin inasmuch as the standard in a number of the states is that cider vinegar should not contain less than 2 per cent. of extractive matter. It is also stated that cider vinegar *always* gives a precipitate with lead acetate, which is not true of certain abnormal cider vinegars.

The chapter on "Paper and Paper-making Materials" is by R. W. Sindall. The usual physical, chemical and microscopical methods are stated in a general and brief way, so briefly indeed that it is doubtful if this chapter will prove very helpful either to the experienced paper analyst or to the uninitiated. Cautionary remarks regarding the accuracy of results which can be obtained by some of the methods given would have been quite helpful. Thus it is well known that the usual methods for the quantitative determination of starch give very inaccurate results on many classes of paper, so inaccurate indeed that in many instances they are not even approximations.

The methods for the quantitative determination of rosin and for the detection of free acids in paper would seem to need amplification. The same criticism can be made of the method given for the determination of the percentage of various kinds of fiber. A statement covering the maximum, minimum, and average size of the various fibers would have been helpful. There are included microphotographs of the more common paper-making fibers.

Because of the detail of these criticisms the work should not be judged harshly, as a majority of the suggestions do not reflect upon the book as a whole, which is a valuable treatise, as have been the earlier editions, but refer rather to surface faults. The new plan followed in this edition, in which each chapter is written by a specialist, seems particularly worthy

of commendation; uniformity is apparent in weights and measures, nomenclature and abbreviations, and the references, which are fully given, are to original sources. The book is attractively bound.

BERNARD H. SMITH.

KLEINES HANDWÖRTERBUCH DER AGRICULTURCHEMIE. VON MAX PASSON. Leipzig: Wilhelm Engelmann. 1910. Pt. 1, pp. 454; Pt. 2, pp. 415. Unbound, M. 22; bound, M. 25.

The author recognizes in the preface that there are already plenty of books dealing with agricultural analytical methods, also with matters relating to the morphology and recognition of various plant products, and publications supplying the information necessary in answering questions likely to be raised by those engaged in farming. The object was not to attempt to duplicate or pattern after any of these works, but rather to bring together from various sources such information as gave promise of placing within reasonably small compass the information which a student of agricultural chemistry would be most likely to need. He has endeavored also to render available matter bearing upon a multitude of questions which those connected with agricultural experiment stations are continually being called upon to answer, and which might otherwise involve a search of many volumes.

The book not only meets such needs but also serves the purpose, for the student in this country, of a German agricultural technical lexicon wherein may be found certain terms common in German works but frequently not defined and unfamiliar to those whose acquaintance with technical German is limited. Perhaps as typical illustrations of the latter, one might mention "Hochmoorboden," "Niederungsmoor" and "Ammoniaksuperphosphat."

The work contains material relating to the more important soil-forming minerals, soils, soil amendments, fertilizers, products of plant life, etc., together with methods for the examination and quantitative determination of many of the more important substances of an agricultural nature and origin. It contains many illustrations, some of which are taken from an earlier well-known work by König, and from other sources.

In the selection of material the author has unfortunately confined himself closely to German sources and might have made the work more valuable and complete had he drawn in some instances on material available elsewhere in Europe, as well as in Japan and the United States.

H. J. WHEELER.

PRODUCER GAS-FIRED FURNACES. By OSKAR NAGEL, PH.D., Consulting Chemical Engineer. New York: Oskar Nagel, P. O. Box 385. pp. 192. Price, \$2.

This deals exhaustively with the production of producer

gas—the construction of producers, the combustion of the gas, and its application to the industries. This includes bone-black, gas retort, muffle, roasting, reverberatory, crucible, and enameling furnaces; in addition to these, the specific applications of producer gas to the iron and steel, the copper and zinc, the lime and cement, and glass industries are carefully discussed. Lastly there is a useful chapter on refractories used in these various furnaces.

The book is profusely illustrated—enough to give a good idea of the various furnaces, but hardly more—and is a valuable contribution to the literature and should be owned by all interested in the subject.

A. H. GILL.

DIE ELEKTROMOTORISCHEN KRÄFTE DER POLARISATION, UND IHRE MESSUNG MIT HILFE DES OSZILLOGRAPHEN. VON M. LE BLANC. Abhandlungen der Deutschen Bunsen-Gesellschaft für angewandte physikalische Chemie. Halle, a/S.: Verlag von Wilhelm Knapp. 1910. pp. 79. Preis, m. 3.00; für mitglieder, m. 1.50.

The earlier work of LeBlanc on the electromotive force of polarization, or "decomposition values" of acids, bases and salts, is one of the most important contributions to physical chemistry in the nineties. It was this work which showed the untenability of the theory of electrolysis which held sway for more than a half century.

This investigation not only pointed out that the old theory of electrolysis contained within itself a self-evident contradiction, but also gave us a satisfactory theory in terms of which the facts in connection with the decomposition of acids, bases and salts by the current could be interpreted. Indeed, it went farther and furnished us with the experimental proof of the new theory of electrolysis—a proof so comprehensive and convincing as scarcely to have been questioned in recent years.

LeBlanc has now extended these earlier investigations, using the oscillograph to measure electromotive force.

H. C. J.

# AMERICAN CHEMICAL JOURNAL

## ON THE PREPARATION OF CERTAIN SULPHONIC ACIDS IN THE FREE STATE.

BY J. H. KASTLE.

Our knowledge of strong acids is limited to a comparatively small group of substances. It is, therefore, a matter of some importance to devise methods whereby the number of such acids may be increased and our knowledge of them extended. The sulphonic acids furnish us with the largest class of strong acids known at present. Unfortunately, most of these can be obtained in the free condition only from their barium, lead or silver salts and this method is so tedious as ordinarily carried out that our knowledge of the acids in the free state is comparatively limited.

In the course of my investigations on this group of substances I have met with two members of the group of aromatic sulphonic acids which can be obtained in beautifully crystalline condition by the simplest possible methods. These

two acids are *p*-nitrotoluenesulphonic acid,  $\text{C}_6\text{H}_4 \begin{matrix} \text{CH}_3 & (1) \\ \text{SO}_2\text{OH} & (2) \\ \text{NO}_2 & (4) \end{matrix}$ ,  
and toluenesulphonic acid, probably the para acid.

The method employed in their isolation in the free condition depends upon the well-known chemical principle that substances containing a common ion show a diminished solubility in the presence of each other. Upon this principle de-



pendes the precipitation of sodium chloride from its aqueous solution by hydrochloric acid and the precipitation of sodium benzenesulphonate from its aqueous solutions by sodium chloride (Gattermann's method of obtaining sodium benzenesulphonate). In the same way certain of the sulphonic acids are precipitated from their concentrated aqueous solutions by another strong acid such as hydrochloric or sulphuric acid. Upon this principle depends the preparation of *p*-nitrotoluenesulphonic and toluenesulphonic acids in the free state.

*p*-Nitrotoluenesulphonic Acid,  $\text{C}_6\text{H}_3 \begin{array}{l} \text{CH}_3 \\ \text{SO}_2\text{OH} \cdot 2\text{H}_2\text{O} \\ \text{NO}_2 \end{array}$ .—In order

to prepare this acid, 50 grams of *p*-nitrotoluene are added to 200 grams of fuming sulphuric acid and the mixture heated on the water bath for a short time to complete the sulphonation. The mixture is then poured into 300 cc. of water and the mixture allowed to cool, when the whole liquid practically solidifies to a thick mass of crystals. This mixture of acid and crystals is then filtered on a platinum cone or a perforated porcelain funnel with the aid of the pump. There are thus obtained 120 grams of moist, granular crystalline acid having much the appearance of brown sugar. This can be recrystallized in the usual manner from hot water. After the third recrystallization the acid was found to contain small amounts of sulphuric acid. A saturated aqueous solution of *p*-nitrotoluenesulphonic acid, prepared as above described, is readily precipitated in the form of the dihydrate by means of concentrated hydrochloric acid. On the addition of an equal volume of concentrated hydrochloric acid to a concentrated aqueous solution of *p*-nitrotoluenesulphonic acid, the solution sets to a thick mass of pearly plates or scales, which, after filtration and drying in the air, have a soapy, unctious feel. After the second or third precipitation by means of concentrated hydrochloric acid, the acid was found to be free from sulphuric acid and on recrystallizing it from water by allowing the concentrated aqueous solution to slowly evaporate at ordinary temperatures the dihydrate was obtained in the form of beautiful, transparent, light yellow prisms of



large size. These have been shown by one of my students in the Kentucky State University, Mr. C. W. Haynes, to contain two molecules of water of crystallization and not two and one-half molecules, as given by Jenssen.

The acid precipitated from its concentrated aqueous solution by concentrated hydrochloric acid is also the dihydrate, since 0.2532 gram of the acid required 0.0399 gram sodium hydroxide for neutralization; the calculated amount for

$\text{C}_6\text{H}_3 \begin{array}{l} \nearrow \text{CH}_3 \\ \text{—} \text{SO}_2\text{OH} \cdot 2\text{H}_2\text{O} \\ \searrow \text{NO}_2 \end{array}$  is 0.0400 gram.

In order, therefore, to obtain the dihydrate of *p*-nitrotoluenesulphonic acid in pure condition, sulphonate *p*-nitrotoluene with fuming sulphuric acid, pour the product of the sulphonation into about an equal volume of water, allow the mixture to cool, filter off the crystals on the pump and purify by solution in water, precipitation with concentrated hydrochloric acid and recrystallization of the product several times from water. For purposes of illustration and study this acid affords an excellent example of the whole group of aromatic sulphonic acids and even for the preparation of the salts and other derivatives of this acid it is a great saving of time to start with the acid prepared in this manner, rather than to prepare these substances from the calcium or barium salt, as is usually done.

*Toluenesulphonic Acid*.—This acid may be obtained in the free condition in precisely the same way as the *p*-nitrotoluenesulphonic acid. It was prepared by adding 100 cc. of toluene in small amounts at a time to 200 cc. of commercial sulphuric acid, sp. gr. 1.84, with constant shaking. When the toluene had all dissolved the mixture was poured into 120 cc. of water and the mixture allowed to cool. Large prismatic crystals of toluenesulphonic acid (probably the para acid), some of them one to two inches in length, separate on cooling. The yield is practically quantitative. A quantity of these crystals was dissolved in the smallest possible amount of warm water. On cooling a considerable amount of the acid again separated in the form of prismatic crystals. These were

filtered off and the filtrate, which was saturated with the toluenesulphonic acid at ordinary temperature, was divided into two parts of 55 cc. each. To one of these portions was added 100 cc. of concentrated hydrochloric acid and to the other 50 cc. In both cases the solution instantly set to a thick paste of crystals. These solutions containing the crystals were then heated, when the crystals dissolved, and on allowing the solutions to stand overnight good crops of large crystals of the toluenesulphonic acid were obtained. These were filtered off and were found to contain small amounts of sulphuric acid, and after drying in a desiccator over solid caustic soda, overnight, they showed traces of hydrochloric acid with silver nitrate. They were then dissolved in the smallest possible amount of water, two volumes of concentrated hydrochloric acid added and the paste of crystals thus obtained dissolved by warming. The solution thus obtained was again allowed to stand overnight when aggregates of large, colorless prismatic crystals, many of them one to one and a half inches in length, separated from the solution. These were found to be free from sulphuric acid. After drying in a desiccator over solid caustic soda for two months these crystals appeared to be absolutely dry, but still were found to contain traces of hydrochloric acid. It would seem, therefore, that the last traces of free hydrochloric acid can be removed only by recrystallization from water. The toluenesulphonic acid obtained by this method appears to be a monohydrate. Thus 0.7160 gram of the acid which had stood two months over solid caustic soda required 0.1521 gram sodium hydroxide for neutralization. For the monohydrate 0.1506 gram would be required, whereas the anhydrous acid would require 0.1664, and the dihydrate 0.1376 gram. It is evident also that the single molecule of water of crystallization which this hydrate contains cannot be removed by drying over solid caustic soda. It is more than likely that the acid with which we are here dealing is the para compound. This, however, has not as yet been proven experimentally. One would certainly be inclined to believe *a priori*, I think, that the method above described for the isolation of these two sulphonic acids would be a general

one for the entire group of aromatic sulphonic acids. Such, however, has unfortunately not proven to be the case. For example, I have failed to isolate benzenesulphonic and *o*-nitrotoluenesulphonic acids by this method. Thus when the product of the sulphonation of benzene, resulting from heating benzene for several days with commercial sulphuric acid, under a reflux condenser, was mixed with water in the proportion of 0.5, 1, 2, 3 and 4 volumes of water to 1 volume of the acid mixture, there was no formation of any crystals even after long standing, and all of my experiments with *o*-nitrotoluenesulphonic acid have resulted negatively. The failure to obtain these acids is doubtless due to a greater solubility of these two acids in sulphuric acid, dilute and concentrated, than holds for toluenesulphonic and *p*-nitrotoluenesulphonic acids.

I am still inclined to believe, however, that a large number of aromatic sulphonic acids can be isolated in the free condition by this method. The fact that *p*-nitrotoluenesulphonic acid can be obtained so easily and that in the form of the dihydrate is such a well-defined chemical species opens up a number of new lines of investigation on the solubility of this acid in various acid mixtures which, with the aid of my students, I hope to follow as soon as the opportunity presents itself.

UNIVERSITY OF VIRGINIA,  
September, 1910.

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## SEVERAL ACIDS SUITABLE FOR USE AS STANDARDS IN ACIDIMETRY.

BY J. H. KASTLE.

In view of the fact that *p*-nitrotoluenesulphonic acid,  $\text{C}_6\text{H}_3 \begin{matrix} \text{CH}_3 & (1) \\ \text{SO}_2\text{OH} & (2) \\ \text{NO}_2 & (4) \end{matrix}$ , is completely ionized in aqueous solution and in view of the ease with which it may be obtained in a beautifully crystalline condition, it occurred to the writer that possibly it could be used to advantage as a standard in acidimetry.

I, therefore, suggested to one of my students in the Kentucky State University, Mr. Haynes,<sup>1</sup> that he undertake an investigation of this acid with this object in view. Accordingly he prepared a standard solution of sodium hydroxide, containing 5.66 milligrams per cc., by titration against a standard solution of sulphuric acid, the exact concentration of which had been determined gravimetrically in the usual manner. Weighed amounts of *p*-nitrotoluenesulphonic acid, which had been carefully purified by several crystallizations from water,<sup>2</sup> were then titrated with this standard solution of sodium hydroxide, using phenolphthalein as the indicator, with the following results:

Quantity of acid used, in grams.	Sodium hydroxide required, in cc.	Milligrams of sodium hydroxide per cc.
0.2000	5.61	5.632
0.3000	8.40	5.642
0.2998	8.38	5.653
0.6535	18.26	5.654
0.3993	11.15	5.658
0.3637	10.14	5.666
0.2172	6.08	5.643
<hr/>		
Total, 2.4335	68.02	39.548
		Average, 5.65

Hence, according to his findings, 1 gram of *p*-nitrotoluenesulphonic acid requires 0.1582 gram of sodium hydroxide for neutralization; the calculated amount is 0.1580 gram.

During the course of this investigation Mr. Haynes observed that, as ordinarily obtained by precipitation from its solutions in fuming sulphuric acid by water and recrystallization from water, *p*-nitrotoluenesulphonic acid contains two molecules of water of crystallization and not two and one-half molecules as found by Jenssen.<sup>3</sup> Thus he found that on drying at 125° to 130° C., 0.3370 gram of the hydrated acid lost 0.0485 gram (14.39 per cent.) and that when heated again

<sup>1</sup> "Some Methods of Standardizing Acid and Alkali Solutions." Thesis for the degree of Bachelor of Science in Chemistry, by C. W. Haynes, State College of Kentucky, 1905.

<sup>2</sup> For details concerning the preparation of *p*-nitrotoluenesulphonic acid, see the preceding paper.

<sup>3</sup> Ann. Chem. (Liebig), **172**, 230.

for half an hour at this temperature there was no further loss of weight. In another experiment he found that 0.4000 gram of the hydrated acid gradually lost, on heating for seven hours at  $123^{\circ}$  to  $131^{\circ}$ , 0.0570 gram (14.25 per cent.) and that on heating one hour longer it suffered no further loss of weight. The calculated value for two molecules of water is 14.23 per cent., whereas for two and one-half molecules it is 17.17 per cent. It follows, therefore, that the modification of the acid with which we were dealing was the dihydrate. Obviously the results of Mr. Haynes's titrations of this acid with standard sodium hydroxide are also in harmony with this conclusion. About this time, *viz.*, 1905, my chemical work was diverted somewhat from its usual channels with the result that these observations made by Mr. Haynes, while working under my direction, were never published.

My attention has again been directed to the subject, however, by reason of the fact that in the course of certain investigations now being carried out in this laboratory I have recently had occasion to prepare and examine two other acids which possess in high degree those characteristics required of standards for use in acidimetry. These are the monopotassium salt of *o*-nitro-*p*-sulphobenzoic acid,  $\text{C}_6\text{H}_3$   $\begin{matrix} \text{COOH} \\ \text{NO}_2 \\ \text{SO}_2\text{OK} \end{matrix}$  (*o*),

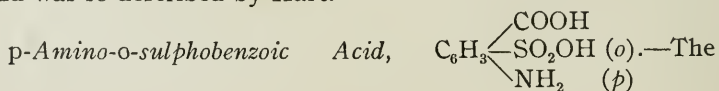
and *p*-amino-*o*-sulphobenzoic acid,  $\text{C}_6\text{H}_3$   $\begin{matrix} \text{COOH} \\ \text{SO}_2\text{OH} \\ \text{NH}_2 \end{matrix}$  (*o*), both of which were first obtained by Hart<sup>1</sup> in the course of an experimental study of the nitrosulphobenzoic acids and some of their derivatives. I have, therefore, deemed it advisable to propose these two acids as standards in acidimetry and to include a few determinations of my own on *p*-nitrotoluenesulphonic acid, in addition to the results obtained by Mr. Haynes, as given above. For the preparation of these two compounds, I have made use of the following methods, based for the most part on Hart's original observations.

Monopotassium *o*-Nitro-*p*-sulphobenzoate,  $\text{C}_6\text{H}_3$   $\begin{matrix} \text{COOH} \\ \text{NO}_2 \\ \text{SO}_2\text{OK} \end{matrix}$  (*o*).—

<sup>1</sup> THIS JOURNAL, 1, 340-356 (1879-80).



In order to prepare this compound, *o*-nitrotoluene is sulphonated by adding it gradually to fuming sulphuric acid, in the proportion of one or two volumes of acid to every volume of *o*-nitrotoluene used, and heating the mixture on the water bath for a few minutes to complete the sulphonation. The mixture is then largely diluted with water, heated nearly to boiling, neutralized with chalk and filtered while hot from the calcium sulphate. The calcium in the hot filtrate is then exactly precipitated with potassium carbonate and the calcium carbonate removed by filtration. The filtrate containing the potassium salt of *o*-nitro-*p*-toluenesulphonic acid is then evaporated to crystallization. On cooling this salt separates in needle-shaped crystals or in pearly, lustrous scales. This salt is then converted into the potassium salt of *o*-nitro-*p*-sulphobenzoic acid by oxidizing with potassium permanganate in alkaline solution. Ten parts by weight of the potassium salt of *o*-nitro-*p*-toluenesulphonic acid and 3 parts by weight of potassium hydroxide are dissolved in 500 parts of water. This solution is then heated on the water bath and 22 parts by weight of finely powdered potassium permanganate added. The mixture is then heated on the water bath for eight to ten hours, at the end of which time a small amount of alcohol is added to decompose any permanganate remaining unchanged. The mixture is then filtered and the clear golden yellow filtrate evaporated to small bulk, when it is allowed to cool and then strongly acidified with concentrated hydrochloric acid. The acid potassium salt of *o*-nitro-*p*-sulphobenzoic acid is thus obtained in the form of anhydrous, prismatic plates which are purified by crystallization from hot water, after the addition of animal charcoal. The salt employed in this investigation was beautifully crystalline, highly refractive, transparent, white to very slightly yellowish and on pulverization yielded a white powder. On heating for one hour in the air bath at 130°–158° the salt showed no loss of weight. It is therefore anhydrous and was so described by Hart.





starting point in the preparation of this acid is the acid potassium salt of *p*-nitro-*o*-sulphobenzoic acid,  $C_6H_3 \begin{cases} \text{COOH} \\ \text{SO}_2\text{OK} \text{ (}o\text{)} \\ \text{NO}_2 \text{ (}p\text{)} \end{cases}$ .

$H_2O$ , which in turn is obtained from *p*-nitrotoluene by sulphonation with fuming sulphuric acid and oxidation with alkaline permanganate according to the directions given by Hart<sup>1</sup> and Kastle.<sup>2</sup> In order to obtain the *p*-amino-*o*-sulphobenzoic acid, the acid potassium salt of *p*-nitro-*o*-sulphobenzoic acid prepared according to Kastle's directions is dissolved in a considerable excess of strong ammonia and the solution saturated with hydrogen sulphide. The solution is then evaporated to dryness on the water bath and the residue is extracted with a small amount of hot water and filtered to remove the sulphur. Hydrochloric acid is then added to the filtrate, when the *p*-amino-*o*-sulphobenzoic acid separates on cooling in the form of delicate, white needles, which are anhydrous. The compound can be purified by crystallization from boiling water containing animal charcoal.

The quantities of sodium hydroxide required to neutralize known amounts of these two compounds and of *p*-nitrotoluenesulphonic acid were then determined in the following manner. Approximately 0.1 N solutions of hydrochloric acid and sodium hydroxide were prepared; 50 cc. of the solution of hydrochloric acid required 50.5 cc. of the solution of sodium hydroxide for neutralization, phenolphthalein being used as the indicator. Duplicate gravimetric determinations of the amount of hydrochloric acid in 50 cc. portions of the solution gave 0.7261 and 0.7259 gram silver chloride, respectively.

Hence, 1 cc. of the solution of hydrochloric acid contains 0.00369412 gram acid and 1 cc. of the solution of sodium hydroxide contains 0.00401258 gram base. Weighed amounts of the three acids here under investigation, the *p*-nitrotoluenesulphonic acid air-dried, the other two, first air-dried and then dried for an hour at 110° in the air bath, were then dissolved in water and titrated with the solution of sodium

<sup>1</sup> *Loc. cit.*, pp. 349-352.

<sup>2</sup> *THIS JOURNAL*, 11, 179 (1889).

hydroxide, phenolphthalein being used as the indicator, with the following results:

Acid.	Quantity of acid taken, in grams.	Sodium hydroxide required for neutralization, in cc.	0.1 N Sodium hydroxide required for neutralization, in cc. (Calc., 50)	Quantity of sodium hydroxide found to be required for neutralization, in grams. (Calc., 0.20004)
<i>p</i> -Nitrotoluenesulphonic	1.2658	49.95	50.097	0.200428
<i>p</i> -Amino- <i>o</i> -sulphobenzoic	0.5428	49.85	49.997	0.200027
Monopotassium <i>o</i> -nitro- <i>p</i> -sulphobenzoate	1.4260	50.00	50.147	0.200629

The several quantities of sodium hydroxide required to neutralize 1 gram of each of these acids, together with the calculated amounts, are as follows:

Acid.	Sodium hydroxide required to neutralize 1 gram of acid, in grams.	
	Found.	Calculated.
<i>p</i> -Nitrotoluenesulphonic	0.1582 (Haynes) 0.1583 (Kastle)	0.15803
<i>p</i> -Amino- <i>o</i> -sulphobenzoic	0.36851	0.36853
Monopotassium <i>o</i> -nitro- <i>p</i> -sulphobenzoate	0.1407	0.14028

For all practical purposes, and it is only for such purposes that these standard acids are recommended, the slight differences between the found and calculated values of the several amounts of sodium hydroxide required to neutralize these three acids are of no significance and in the case of one of them at least, *viz.*, the *p*-amino-*o*-sulphobenzoic acid, the agreement is such as to meet the most exact requirements of volumetric analysis.

To review briefly the properties which render these compounds of value as standards in acidimetry: We see that each of them is a very definite and well-defined chemical species. They are all easily prepared and are readily obtained in perfectly pure condition. Two of them, *viz.*, *p*-amino-*o*-sulphobenzoic acid and monopotassium *o*-nitro-*p*-sulphobenzoate are anhydrous and, hence, can be thoroughly dried in the air

and also by the aid of heat or in the desiccator over sulphuric acid, without danger of alteration in composition. All of them are stable in the air under ordinary conditions, none of them are hygroscopic or deliquescent. All of them give very sharp end reactions with phenolphthalein, one drop of 0.1 N sodium hydroxide being sufficient to change the color of the titer from colorless to pink. As shown by Mr. Haynes, *p*-nitrotoluenesulphonic acid crystallizes with two molecules of water of crystallization. It is obviously open to the objections which have been urged against all hydrates as chemical standards, such as danger of occluded mother liquor, difficulty of drying without loss of water of hydration, etc. On the other hand, this particular compound is very definite and stable under ordinary atmospheric conditions, showing great tendency to crystallize. It is completely ionized at ordinary dilutions.

Its reaction towards indicators is particularly sharp and definite, so that in my opinion it has much to commend it as a standard in acidimetry, despite the fact that it is hydrated.

UNIVERSITY OF VIRGINIA,  
August, 1910.

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[Contributions from the Sheffield Laboratory of Yale University.]

## CLXXXVI.—ON IODINE DERIVATIVES OF TOLUENE.

BY HENRY L. WHEELER.

EXPERIMENTAL WORK BY CHARLES A. BRAUTLECHT AND CHARLES HOFFMAN.

There are nineteen nucleus-substituted iodine derivatives of toluene: three mono-, six di-, six tri-, three tetra- and one penta-iodtoluenes.

When the work on iodtoluenes was started in this laboratory only two of these polyiod derivatives of known structure had been described. 2,6-Diiodtoluene had been prepared by Cohen and Miller<sup>1</sup> from the corresponding iodnitrotoluene and 3,4-diiodtoluene had been obtained by Willgerodt and Simonis.<sup>2</sup>

Neumann<sup>3</sup> found that when *o*- or *p*-iodtoluene was heated

<sup>1</sup> J. Chem. Soc., **85**, 1627 (1904).

<sup>2</sup> Ber. d. chem. Ges., **39**, 269 (1906).

<sup>3</sup> Ann. Chem. (Liebig), **241**, 50 (1887).

with sulphuric acid a di- and a triiodtoluene were formed. For no reason, otherwise than that he started with an *o*- or *p*-iodtoluene, these products were considered to have iodine atoms in these positions and to be 2,4-diiod- and 2,4,6-triiodtoluenes.

We have prepared 2,4-diiodtoluene from 2,4-dinitrotoluene by alternately reducing the nitro groups and replacing the amino groups by iodine. We obtained an oil with the properties described by Neumann; his assumption was therefore correct in this case. Ortho- and metaiodtoluenes are the only other members of this series that are oils at ordinary temperature.

In regard to the triiodtoluene, which was prepared according to his directions, it was noticed that the substance has the same melting point ( $118^{\circ}$ – $119^{\circ}$ ) as 2,4,5-triiodtoluene, and this triiodtoluene we have prepared by three different methods. When the substances were mixed the melting point was not altered. On the other hand, when Neumann's triiodtoluene was mixed with 2,4,6-triiodtoluene, prepared from 2,4,6-triiod-*m*-toluidine, the mixture melted at  $75^{\circ}$ – $85^{\circ}$ . The triiodtoluene in question is therefore 2,4,5- and not 2,4,6-triiodtoluene.

2,4-Dichlor- and 2,4,5-trichlortoluenes are the main products formed on chlorinating toluene.<sup>1</sup>

In our paper on the action of iodine on *p*-toluidine we described 2,3-diiodtoluene, 3,5-diiodtoluene and 3,4,5-triiodtoluene<sup>2</sup> and our article on the action of iodine on *o*-toluidine contained a description of 2,5-diiodtoluene,<sup>3</sup> while the investigation of the action of iodine on *m*-toluidine led to the preparation of 2,3,6-triiodtoluene, 3,4,6-triiodtoluene and 2,3,4,6-tetraiodtoluene.<sup>4</sup>

In this paper we describe the remaining nucleus-substituted iodine derivatives of toluene required by theory. The methods used for their preparation were as follows: We found that

<sup>1</sup> Cohen and Dakin: J. Chem. Soc., **81**, 1340 (1902).

<sup>2</sup> THIS JOURNAL, **42**, 441 (1909).

<sup>3</sup> *Ibid.*, **42**, 498

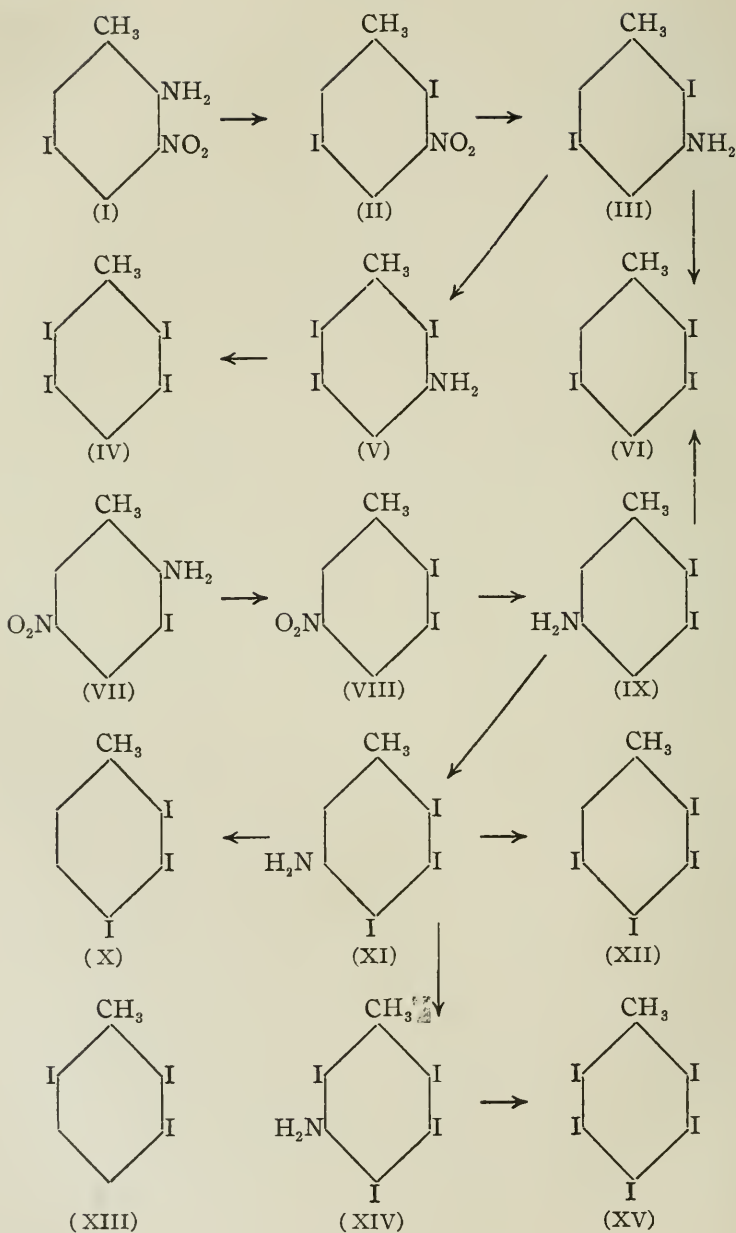
<sup>4</sup> *Ibid.*, **44**, 126 (1910).

3-nitro-*o*-toluidine is attacked by iodine monochloride in the 5-position, giving 5-iod-3-nitro-*o*-toluidine (I), while 5-nitro-*o*-toluidine gives 3-iod-5-nitro-*o*-toluidine (VII). This was shown by replacing the amino groups in these compounds by iodine. The resulting 2,5-diiod-3-nitrotoluene (II) and 5,6-diiod-3-nitrotoluene (VIII) were reduced to 2,5-diiod-*m*-toluidine (III) and 5,6-diiod-*m*-toluidine (IX). Then by means of the diazo reaction a triiodtoluene melting at  $72^{\circ}$ – $73^{\circ}$  was obtained from both of these toluidines. Since the products obtained by these two methods proved to be identical, and this compound was not identical with 2,3,6-triiodtoluene (XIII), melting at  $80^{\circ}$ .5, it was therefore 2,3,5-triiodtoluene (VI).

When 5,6-diiod-*m*-toluidine (IX) was treated with iodine the hydrogen in the 4-position was first substituted. This was shown on removing the amino group from the triiodtoluidine (XI) thus formed, whereupon a triiodtoluene (X), melting at  $92^{\circ}$ , was obtained. This was different from 2,3,6-triiodtoluene (XIII) from 2,6-diiod-*m*-toluidine. This 2,3,6-triiodtoluene would result if the substitution in 5,6-diiod-*m*-toluidine took place in the 2-position. The triiodtoluene obtained in this case was therefore 2,3,4-triiodtoluene (X).

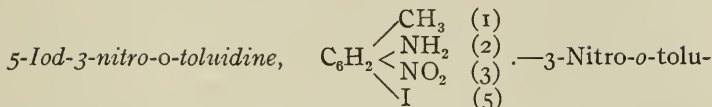
On this fact is also based the structure of 2,3,4,5-tetraiodtoluene (XII) prepared from the triiodtoluidine (XI) by replacing the amino group by iodine, and, since by the action of iodine on 2,5-diiod-*m*-toluidine (III) a triiod-*m*-toluidine (V) results, which gives a different tetraiodtoluene (IV), it follows that 2,5-diiod-*m*-toluidine (III) is attacked in the 6-position or para to the amino group, the product in this case being 2,5,6-triiod-*m*-toluidine (V), and the tetra derivative from this is 2,3,5,6-tetraiodtoluene (IV).

Both 4,5,6-triiod-*m*-toluidine (XI) and 2,5,6-triiod-*m*-toluidine (V) are further acted on by iodine and a tetraiodtoluene is formed. The products in these two cases were identical, as required by theory, and when the amino group in this compound was diazotized and replaced by iodine pentaiodtoluene (XV) was obtained.



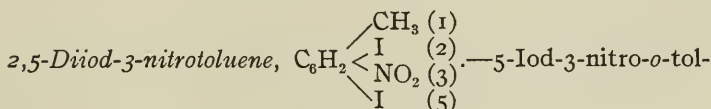


BY CHARLES A. BRAUTLECHT.



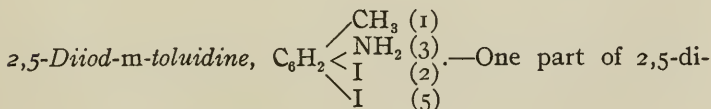
idine was prepared by nitrating *o*-acettoluide in the manner described by Reverdin and Crépieux.<sup>1</sup> Twenty-two and a half grams of this compound were suspended in 20 grams of glacial acetic acid and 24.5 grams of iodine monochloride were added. The reaction takes place with evolution of heat but nevertheless the mixture was warmed to boiling for a few minutes. It was then treated with dilute sodium hydroxide and hot water. The yield of crude 5-iod-3-nitro-*o*-toluidine was 39.7 grams or 98 per cent. of the calculated. It crystallized from alcohol in orange needles melting at 135°. It is difficultly soluble in water and easily in hot alcohol.

	Calculated for $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{I}$ .	I.	Found.
N	10.07	9.88	10.03



uidine was mixed with 4 parts of concentrated sulphuric acid, cooled in a freezing mixture, and a half part of dry powdered sodium nitrite added. When the whole was poured on cracked ice, an almost complete solution resulted. The filtered diazo solution was then treated with 3.5 parts of potassium iodide dissolved in a little ice water. The yield of crude diiodnitrotoluene obtained on warming the solution, averaged, as the result of seven experiments, about 81 per cent. of the calculated. When the material was crystallized from alcohol we obtained colorless prisms melting, to an oil, at 95°.

	Calculated for $\text{C}_7\text{H}_5\text{O}_2\text{NI}_2$ .	I.	Found.
N	3.60	3.49	3.52

<sup>1</sup> Ber. d. chem. Ges., **33**, 2498.

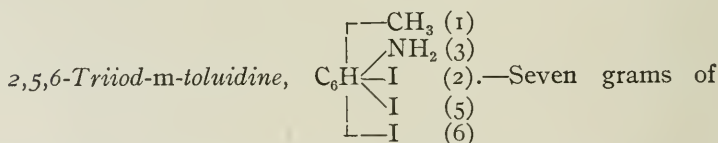
iod-3-nitrotoluene was reduced by warming for several hours with a mixture of 8 parts hydrated ferrous sulphate and 20 parts of concentrated ammonium hydroxide diluted with 8-20 parts of water. On filtering and extracting the residue with alcohol the yield of crude material was usually about 60 per cent. of the calculated. When crystallized from alcohol, after boiling with animal charcoal, pale brown prisms, melting at  $82^{\circ}$ , were obtained.

	Calculated for $C_7H_7NI_2$ .	Found.
I	70.75	70.62

When this substance was diazotized and the solution treated with potassium iodide, in the usual manner, the product crystallized from alcohol in buff-colored plates. They melted at  $72^{\circ}$ - $73^{\circ}$  and proved to be identical with 3,5,6- (or 2,3,5-) triiodtoluene prepared by Hoffman from 5,6-diiod-*m*-toluidine (see below). This fact has served to determine the structure of this and the related iodine derivatives. This triiodtoluene is practically nonvolatile in steam. Two and a half liters of distillate contained about 0.05 gram.

2,5-Diiod-*m*-acettoluide,  $C_6H_2CH_3I_2NHCOCH_3$ , from the base and acetic anhydride, crystallized from alcohol, in which it is moderately soluble, in long, colorless, feltlike needles, melting at  $198^{\circ}$ - $199^{\circ}$ . It is practically insoluble in water.

	Calculated for $C_9H_9ONI_2$ .	Found.
N	3.49	3.47

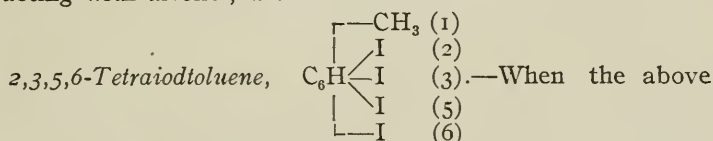


2,5-diiod-*m*-toluidine, 5 grams of iodine, 4 grams of calcium carbonate, 20 cc. of ether and 15 cc. of water were warmed on the steam bath for 18 hours. The ether was evaporated, the solution filtered and the residue extracted with alcohol; on concentrating the alcoholic solution about 50 per cent. of the calculated amount of triiod-*m*-toluidine separated. When

crystallized from alcohol it formed colorless needles which melted sharply at  $119^{\circ}$ – $120^{\circ}$ .

	Calculated for $C_7H_6NI_3$ .	Found.
N	2.89	2.87

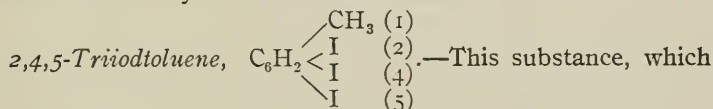
When four atomic proportions of iodine were used in the above experiment 10 grams of 2,5-diiod-*m*-toluidine gave a mixture of about equal parts of 2,5,6-triiod-*m*-toluidine and 2,4,5,6-tetraiod-*m*-toluidine, melting at  $205^{\circ}$  and described by Hoffman below. The compounds were obtained by first extracting with alcohol, then with acetic acid or benzene.



2,5,6-triiod-*m*-toluidine was diazotized in the usual manner, a noticeable quantity of material remained undissolved. On treating the clear diazo solution with potassium iodide the yield, in two experiments, was 64 per cent. of the calculated. The product was crystallized from benzene; it then formed colorless, arborescent needles melting to a clear oil at  $125^{\circ}$ . It was less soluble in alcohol than in benzene.

	Calculated for $C_7H_4I_4$ .	Found.
I	85.23	84.53

Since this tetraiodtoluene is different from the tetraiodtoluene (melting at  $284^{\circ}$ ) obtained by Hoffman (below) from 4,5,6-triiod-*m*-toluidine, it follows that this must be the 2,3,5,6-derivative and that 2,5-diiod-*m*-toluidine iodates in the 6-position or para to the amino group, otherwise the two methods should yield the same tetraiodtoluene.



may be considered as 3,4,6-triiodtoluene, was described in one of our previous papers.<sup>1</sup> It was prepared from 4,6-diiod-*m*-toluidine. We have now prepared the same sub-

<sup>1</sup> THIS JOURNAL, 44, 140 (1910).

stance in two other ways, namely from *p*-iod-*o*-toluidine and from *p*-nitro-*o*-toluidine.

4,5-Diod-*o*-toluidine,  $\text{C}_6\text{H}_2$   $\begin{matrix} \text{CH}_3 & (1) \\ & \text{NH}_2 & (2) \\ & \text{I} & (4) \\ & \text{I} & (5) \end{matrix}$ .—This was obtained by

the action of iodine, or better by the action of iodine monochloride, on *p*-iod-*o*-toluidine in glacial acetic acid. After adding water and then washing the precipitate with dilute alkali it crystallized from alcohol in stout needles or long, colorless prisms. It melted constantly at  $85^\circ$ .

	Calculated for $\text{C}_7\text{H}_7\text{NI}_2$ .	Found.
N	3.90	3.86

When this material was diazotized in the usual manner and the solution treated with potassium iodide, the triiodtoluene obtained, after crystallizing from alcohol, melted at  $118^\circ$ – $119^\circ$ , and when mixed with 3,4,6-triiodtoluene the melting point was not lowered.

4 - Nitro - 5 - iod - o - toluidine,  $\text{C}_6\text{H}_2$   $\begin{matrix} \text{CH}_3 & (1) \\ & \text{NH}_2 & (2) \\ & \text{NO}_2 & (4) \\ & \text{I} & (5) \end{matrix}$ .—Fourteen

grams of *p*-nitro-*o*-toluidine were dissolved in glacial acetic acid and allowed to stand for 3 days with 15 grams of iodine monochloride. The crystals which separated were dissolved in water containing a little hydrochloric acid and the solution was poured into aqueous ammonia. Long, bright yellow prisms separated, which, when crystallized from alcohol, melted at  $109^\circ$ . The yield in this experiment was 70 per cent. of the calculated, in others more or less tar was formed.

	Calculated for $\text{C}_7\text{H}_7\text{O}_2\text{N}_2\text{I}$ .	Found.
N	10.07	9.87

2,5-Diod-4-nitrotoluene,  $\text{C}_6\text{H}_2$   $\begin{matrix} \text{CH}_3 & (1) \\ & \text{I} & (2) \\ & \text{I} & (5) \\ & \text{NO}_2 & (4) \end{matrix}$ .—Eighteen grams of

4-nitro-5-iod-*o*-toluidine were diazotized and the solution treated with potassium iodide in excess. This gave 20 grams

of diiodnitrotoluene which, when crystallized from alcohol, in which it is moderately soluble, formed buff-colored prismatic plates, melting sharply at  $117^{\circ}$ .

	Calculated for $C_7H_5O_2NI_2$ .	Found.
N	3.60	3.57

2,5-Diod-*p*-toluidine,  $C_6H_2$   $\begin{matrix} \nearrow CH_3 (1) \\ \nearrow I (2) \\ \nearrow I (5) \\ \searrow NH_2 (4) \end{matrix}$ .—Ten grams of the

above nitro compound were reduced with ferrous sulphate and ammonia in the usual manner. The product was extracted with alcohol and on concentrating and cooling the solution 6 grams of buff-colored prisms were obtained. On recrystallizing from alcohol they melted constantly at  $109^{\circ}$ .

	Calculated for $C_7H_7NI_2$ .	I.	Found.	II.
N	3.90	3.64		3.84

When this substance was diazotized and treated with potassium iodide 2,4,5-triiodtoluene was obtained. This triiodtoluene is identical with the one obtained by Neumann<sup>1</sup> by warming *o*- or *p*-iodtoluene with sulphuric acid.

2,4,6-Triiodtoluene,  $C_6H_2$   $\begin{matrix} \nearrow CH_3 (1) \\ \nearrow I (2) \\ \nearrow I (4) \\ \searrow I (6) \end{matrix}$ .—Neumann's supposed

2,4,6-triiodtoluene was prepared from *p*-iodtoluene according to his directions. It melted at  $118^{\circ}$  and when mixed with 2,4,5-triiodtoluene, prepared by the three different methods given above, the melting point was not lowered. When it was mixed with the true 2,4,6-triiodtoluene from 2,4,6-triiod-*m*-toluidine the mixture melted as low as  $75^{\circ}$ – $85^{\circ}$ . The triiodtoluene prepared by Neumann's method is colorless or has a pale cream color. 2,4,5-Triiodtoluene prepared by our methods has a brownish white color which can be removed by boiling the alcoholic solution with animal charcoal.

Eight and eight-tenths grams of 2,4,6-triiod-*m*-toluidine were dissolved in 30 cc. of concentrated sulphuric acid and cooled in a freezing mixture. To the purple solution 5 grams

<sup>1</sup> Ann. Chem. (Liebig), **240**, 50.

of dry, powdered sodium nitrite were added and the mixture poured upon crushed ice. After standing for a half hour a lemon-colored diazo solution and a bright yellow residue were obtained. The solution was poured into 100 cc. of alcohol and allowed to stand for an hour, then boiled for another hour. Light brown crystalline material separated and when this was filtered off and dried it weighed 2.6 grams, or 31 per cent. of the calculated. It was readily soluble in benzene from which it crystallized in colorless needles. It was difficultly soluble in alcohol and it melted to a clear oil at 105°.

	Calculated for C <sub>7</sub> H <sub>5</sub> I <sub>3</sub> .	Found.
I	81.06	80.49

When the yellow residue which was obtained above was dissolved in sulphuric acid, diazotized a second time, and the solution treated with alcohol, a further quantity (20 per cent. of the calculated) of triiodtoluene was obtained.

BY CHARLES HOFFMAN.

3-Iod-5-nitro-*o*-toluidine,  $C_6H_2 \begin{cases} CH_3 (1) \\ NH_2 (2) \\ I (3) \\ NO_2 (5) \end{cases}$ .—Eight grams of

5-nitro-*o*-toluidine<sup>1</sup> were dissolved in 55 cc. of glacial acetic acid and to this solution 13 grams of iodine monochloride (1 mol.) were slowly added, with constant shaking. The mixture became warm and a brown precipitate soon separated after all the monochloride was added. The mixture was then heated for an hour under a return condenser. A solution of acid sodium sulphite was added and the solid substance which separated was filtered, washed and dried. The yield was 13.7 grams, or 90 per cent. of the calculated. The crude product melted at 171° and when crystallized twice from alcohol it gave long, brown prisms, melting to a clear oil at 173°. The material was insoluble in water, alkali and dilute acids, but readily soluble in alcohol and benzene. The action of 2 molecular proportions of iodine monochloride on 5-nitro-*o*-toluidine gave the same compound.

<sup>1</sup> Reverdin and Crépeux: Ber. d. chem. Ges., **33**, 2498.



	Calculated for $C_7H_7O_2N_2I$ .	Found.
N	10.08	10.24

2,3-Diiod-5-nitrotoluene,  $C_6H_2$   $\begin{matrix} \nearrow CH_3 (1) \\ \nearrow I (2) \\ \nearrow I (3) \\ \searrow NO_2 (5) \end{matrix}$ .—Five grams of

3-iod-5-nitro-*o*-toluidine were dissolved in 10 cc. of cold, concentrated sulphuric acid and to this solution 2.5 grams of finely powdered dry sodium nitrite were added at 0°. The brown, pasty mixture was poured on finely crushed ice, whereupon a light brown solution was obtained. The diazo solution, after standing a half hour, was filtered from a small amount of undissolved material into a flask containing an ice-cold solution of 20 grams of potassium iodide. A brownish-red diazo iodide separated which decomposed upon heating, giving off nitrogen. The dark substance, containing iodine, was decolorized by means of acid sodium sulphite. The crude product then weighed 6.4 grams, or 93 per cent. of the calculated. From alcohol it formed long, prismatic, light brown needles and it melted to an oil at 143°. It is moderately soluble in hot alcohol, readily soluble in cold benzene, difficultly soluble in petroleum ether and water.

	Calculated for $C_7H_5O_2NI_2$ .	Found.
N	3.60	3.53

5,6-Diiod-*m*-toluidine,  $C_6H_2$   $\begin{matrix} \nearrow CH_3 (1) \\ \nearrow NH_2 (3) \\ \nearrow I (5) \\ \searrow I (6) \end{matrix}$ .—Twenty-five grams

of the above 2,3-diiod-5-nitrotoluene or 5,6-diiod-3-nitrotoluene, 180 grams of ferrous sulphate (10 molecules), 500 cc. of water and 250 cc. of concentrated ammonia were mixed and allowed to stand for 15 hours at 60°. The mixture was then filtered and the residue extracted with alcohol. This gave 14.3 grams of material melting at 105°–106°, which is 62 per cent. of the calculated. Two crystallizations from alcohol produced large, brown, spikelike crystals which melted to an oil at 106°. This compound distilled slowly with steam; it was then obtained colorless, and the melting point was not

changed. It is readily soluble in alcohol and difficultly in petroleum ether and water. With mineral acids it forms salts which are difficultly soluble.

	Calculated for $C_7H_7NI_2$ .	Found.
I	70.75	70.77

*5,6-Diod-m-acettoluide*,  $C_8H_2I_2CH_3NHCOCH_3$ , from the base and acetic anhydride, crystallizes from alcohol in small, spike-like clusters of crystals melting at  $208^\circ$ . It is moderately soluble in alcohol and difficultly soluble in hot water.

	Calculated for $C_9H_9ONI_2$ .	Found.
N	3.49	3.38

*3,5,6-Triiodtoluene*,  $C_6H_2$   $\begin{array}{l} \nearrow CH_3 (1) \\ | I (3) \\ | I (5) \\ \searrow I (6) \end{array}$ .—This was prepared from

5,6-diiod-*m*-toluidine by diazotizing and treating the solution with potassium iodide as described in the case of 2,3-diiod-5-nitrotoluene. 5,6-Diod-*m*-toluidine, like 4,6-diiod-*m*-toluidine, forms a very difficultly soluble sulphate which it is difficult to diazotize by the above method. The sulphuric acid solution of 5 grams of the base, containing an excess of nitrite, after being poured on crushed ice, was allowed to stand for 1 hour, then filtered from unaltered sulphate. The weight of triiodtoluene obtained was 3.5 grams, or 53 per cent. of the calculated. When the material was crystallized from alcohol it formed large, light orange, twinned plates, melting at  $72^\circ$ – $73^\circ$ .

	Calculated for $C_7H_5I_3$ .	Found.
I	81.06	80.30

This compound, which may also be considered as 2,3,5-triiodtoluene, is identical with the triiodtoluene from 2,5-diiod-*m*-toluidine (Brautlecht). When the different preparations were mixed the melting point was not altered.

*4,5,6-Triiod-m-toluidine*,  $C_6H$   $\begin{array}{l} | CH_3 (1) \\ | NH_2 (3) \\ | I (4) \\ | I (5) \\ | I (6) \end{array}$ .—Five grams of 5,6-

diiod-*m*-toluidine were mixed with two molecular proportions of iodine ( $I_4$ ) in the presence of some water, ether and an excess of calcium carbonate. The mixture was warmed on the steam bath under a return condenser for 35 hours. Steam was then passed in until the free iodine was removed. No unaltered diiod-*m*-toluidine distilled over. The substance left in the flask was filtered and the residue was extracted with alcohol. This treatment gave 3 grams of material melting at  $118^\circ$ – $120^\circ$ , which, as triiod-*m*-toluidine, corresponds to 45 per cent. of the diiod-*m*-toluidine. Several crystallizations from alcohol, in which the substance is readily soluble, gave small, brown needles, melting constantly, to a clear oil, at  $122^\circ$ . This base dissolves to only a slight extent in dilute hydrochloric acid.

N	Calculated for	I.	Found.
	$C_7H_5NI_3$ .		II.
	2.89	2.85	2.75

2,4,5,6-Tetraiod-*m*-toluidine,  $C_6 \begin{cases} CH_3 (1) \\ NH_2 (3) \\ I_4 (2,4,5,6) \end{cases}$ . —The residue re-

maining from the above, after three or four extractions with alcohol, was treated with dilute hydrochloric acid to dissolve the calcium carbonate. The residue remaining was filtered and then extracted with glacial acetic acid. We obtained 1.5 grams of a substance corresponding to 18 per cent. of the diiod-*m*-toluidine, crystallizing in small needles, melting at  $185^\circ$ – $195^\circ$ . Three more crystallizations gave a product melting constantly at  $205^\circ$ . This was difficultly soluble in all of the organic solvents and insoluble in dilute acids.

I	Calculated for	Found.
	$C_7H_5NI_4$ .	
	83.14	81.62

4,5,6-Triiod-*m*-acetoluide,  $C_6HCH_3I_3NHCOCH_3$ , from the base and acetyl chloride (acetic anhydride reacts slowly and incompletely), forms colorless needles which melt with effervescence at  $265^\circ$ . It is moderately soluble in alcohol and very difficultly soluble in hot water.

N	Calculated for	Found.
	$C_9H_5ONI_3$ .	
	2.66	2.77

2,3,4-Triiodtoluene,  $\text{C}_6\text{H}_2$   $\begin{array}{l} \text{CH}_3 \text{ (1)} \\ \text{I} \text{ (2)} \\ \text{I} \text{ (3)} \\ \text{I} \text{ (4)} \end{array}$ .—Ten grams of concentra-

ted sulphuric acid were added to 100 cc. of absolute alcohol and three grams of 4,5,6-triiod-*m*-toluidine were dissolved in the warm mixture. We then slowly added three grams of sodium nitrite, waiting each time until the effervescence ceased. After all the nitrite was added the solution was heated for 1 hour on the steam bath and then poured into water. An oily substance separated which, on standing, solidified to a sticky mass. This was boiled in alcoholic solution with animal charcoal, filtered and, on cooling, 1.8 grams, or 62 per cent. of the calculated, of light brown crystals separated. On crystallizing twice more from alcohol radiating bunches of needles were obtained; they then melted constantly at 92°. This triiodtoluene is readily soluble in benzene and moderately soluble in alcohol. When mixed with 2,3,6-triiodtoluene, melting at 80°.5, the mixture melted at 60°–63°. The fact that the compounds are not identical shows that 5,6-diiod-*m*-toluidine iodates in the 4-position and proves the structure of 4,5,6-triiod-*m*-toluidine.

	Calculated for $\text{C}_7\text{H}_5\text{I}_3$ .	Found.
I	81.06	79.16

3,4,5,6-Tetraiodtoluene,  $\text{C}_6\text{H}$   $\begin{array}{l} \text{CH}_3 \text{ (1)} \\ \text{I} \text{ (3)} \\ \text{I} \text{ (4)} \\ \text{I} \text{ (5)} \\ \text{I} \text{ (6)} \end{array}$ .—Three and a half

grams of 4,5,6-triiod-*m*-toluidine were diazotized and the diazo solution filtered from more or less undissolved material into a solution of potassium iodide. The product, after the usual treatment, weighed 2.7 grams, or 63 per cent. of the calculated. This, on crystallizing from benzene, melted to an oil at 284°–285°. It is moderately soluble in benzene and difficultly soluble in alcohol. From the former solvent it separates in straw-yellow needles.

	Calculated for $C_7H_5I_4$ .	Found.
I	85.23	85.63

*Pentaiodtoluene*,  $C_6I_5CH_3$ .—Three and three-tenths grams of the tetraiod-*m*-toluidine were diazotized as in the previous experiments. Considerable (unaltered?) matter remained undissolved and the diazo solution was filtered into that of the potassium iodide. The diazo iodide formed in the filtrate was decomposed by heating and a solid substance separated which was dark but became almost colorless upon adding acid sodium sulphite. The yield was 0.8 gram, or 20 per cent. of the calculated. On recrystallizing this from benzene we obtained small needles having a dull yellow color and melting with decomposition at about  $340^\circ$ . This compound is difficultly soluble in the ordinary solvents.

	Calculated for $C_7H_5I_6$ .	Found.
I	87.95	87.27

NEW HAVEN, CONN.,  
October, 1910.

## NOTE ON AMINOMETHYLBENZOIC ACIDS.

By HENRY L. WHEELER AND CHARLES HOFFMAN.

Since the appearance of our article on "Alkylation of Aromatic Amino Acids: Aminomethylbenzoic Acids" (third paper),<sup>1</sup> Professor Gabriel has had the kindness to call our attention to the work of his students on the nitration of *m*-toluic acid, which we regret to state had been overlooked by us.

Findekle<sup>2</sup> and Müller<sup>3</sup> have shown that the nitro acid formed in chief amount (melting at  $219^\circ$ – $220^\circ$ ) is 2-nitro-3-methylbenzoic acid (*2-Nitro-m-toluylsäure*) as originally stated by Jacobsen,<sup>4</sup> and not the isomer 2-nitro-5-methylbenzoic acid (*4-Nitrotoluylsäure*). The latter structure was assigned to this acid by Panaotovic<sup>5</sup> owing to the similarity in melting points of the corresponding amino acids. The acid is also

<sup>1</sup> THIS JOURNAL, **44**, 113 (1910).

<sup>2</sup> Ber. d. chem. Ges., **38**, 3553 (1905).

<sup>3</sup> *Ibid.*, **42**, 430 (1909).

<sup>4</sup> *Ibid.*, **14**, 2353.

<sup>5</sup> J. prakt. Chem., [2] **33**, 62.

represented in Beilstein's "Handbuch"<sup>1</sup> as having the 2,5-structure (*4-Nitrotoluylsäure*), which we accepted as correct.

Some recent results obtained by us in the study of the structure of this compound will be communicated later. They show that the acid in question is, as Findeklee and Müller state, the 2-nitro-3-methylbenzoic acid and that the 2,5-structure is excluded.

Our supposed 2-amino-3-iod-5-methyl benzoic acid should therefore be viewed as 2-amino-3-methyl-5-iodbenzoic acid, the supposed 2-amino-5-methylbenzoic acid and its derivatives being 2-amino-3-methyl compounds.

NEW HAVEN, CONN.,  
October, 1910.

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## THE CONDUCTIVITY, DISSOCIATION AND TEMPERATURE COEFFICIENTS OF CONDUCTIVITY AT 35°, 50° AND 65° OF AQUEOUS SOLUTIONS OF A NUMBER OF SALTS.

BY A. P. WEST AND HARRY C. JONES.<sup>2</sup>

[FOURTEENTH COMMUNICATION.]

This investigation is the direct continuation of the work of Clover and Jones<sup>3</sup> on the conductivities of a number of inorganic and organic compounds over the above-mentioned range in temperature, and also at a slightly higher temperature.

It is also part of a series of investigations which has been in progress in this laboratory for ten years, and on which thirteen papers<sup>4</sup> have already been published. Of these the papers of Douglas, West, Jacobson, Clover and White deal

<sup>1</sup> III, 1337.

<sup>2</sup> This investigation was carried out with the aid of a grant from the Bache Fund.

<sup>3</sup> THIS JOURNAL, **43**, 187 (1910).

<sup>4</sup> Jones and Douglas: THIS JOURNAL, **26**, 428 (1901). Jones and Getman: *Ibid.*, **27**, 433 (1902). Jones and Getman: Z. physik. Chem., **46**, 244 (1903); Physic. Rev., **18**, 146 (1904). Jones and Getman: THIS JOURNAL, **31**, 303 (1904). Jones and Bassett: *Ibid.*, **33**, 534 (1905). Jones and Bassett: *Ibid.*, **34**, 290 (1905). Jones and West: *Ibid.*, **34**, 357 (1905). Jones: *Ibid.*, **35**, 445 (1906). Jones and Pearce: *Ibid.*, **38**, 683 (1907). Jones and Jacobson: *Ibid.*, **40**, 355 (1908). White and Jones: *Ibid.*, **42**, 520 (1909). Clover and Jones: *Ibid.*, **43**, 187 (1910). White and Jones: *Ibid.*, **44**, 159 (1910).



solely with the problem in question, while the other communications contain data that bear directly upon it.

The problem is to determine the conductivity and dissociation of all of the more common electrolytes, inorganic and organic, at the ordinary temperatures at which chemical reactions take place. The work has been limited thus far to temperatures between  $0^{\circ}$  and  $65^{\circ}$ . We intend, however, to work at temperatures lower than  $0^{\circ}$ . Apparently we cannot work very much above  $65^{\circ}$  on account of the solubility of glass in water at high temperatures, but we may be able to overcome this difficulty.

Such data as we are now obtaining seem especially valuable, since it is over these ranges in temperature that most chemical reactions take place. We know that chemical reactions, in general, are ionic, and one of the first steps toward the understanding of the real meaning of reactions is to know the dissociation of the substances that take part in the reactions.

If we examine the literature we shall find that a fairly large number of conductivity measurements have been recorded. These, however, have been made chiefly at the temperatures  $0^{\circ}$ ,  $18^{\circ}$ , and  $25^{\circ}$ , over a comparatively limited dilution, and embrace only a small part of the compounds with which the chemist has most frequently to deal. Indeed, our experience in searching for data in connection with the conductivity and dissociation of compounds at a given dilution and temperature is that in a large majority of cases the data that are desired are lacking. This applies especially to temperatures above  $25^{\circ}$  for which very few reliable data are available.

Further, the method of determining the conductivity of electrolytes, like scientific methods in general, is improved as time goes on. We have now better induction coils, better Wheatstone bridges, better conductivity cells, and far better rheostats than in the early days of the method. We are thus enabled to obtain more accurate data than formerly for all substances and at all temperatures.

In undertaking this elaborate investigation of the conduc-

tivity and dissociation of electrolytes in general, our first thought has been to secure the best possible apparatus and conditions. The coil used was the most improved form devised by Leeds and Northrup after experimenting a number of years on this problem. The cells were all of the ground-glass stoppered type, which has been used in this laboratory for some years. These cells are made of hard glass and soaked in water and acid a long time before using to diminish the solubility of the glass. The electrodes are tightly sealed into both tops and bottoms of the ground-glass stoppers to prevent the distance between the electrode plates from changing after the cell constants have been determined.

The rheostat used was made by Leeds and Northrup and calibrated both by them and by the Bureau of Standards in Washington.

At the beginning of the work the method and details of manipulation were essentially those used by Clover and Jones,<sup>1</sup> but as the investigation progressed a number of improvements were introduced.

#### *Preparation of Solutions.*

Since we worked over a range of temperature of only 30°, we found it convenient to prepare the solutions at the intermediate temperature, 50°, and then to use the solutions at the three temperatures, 35°, 50° and 65°. But since the volume of a solution varies with the temperature it was, of course, necessary to apply a correction at 35° and 65° to the volume of solutions made up at 50°.

When a standard solution is cooled from 50° to 35° there is a contraction in volume and a consequent increase in the concentration of the solution. The value of  $\mu_v$  for any solution would, therefore, be slightly too large. The value of  $\mu_v$  as found must be multiplied by the factor 0.994 for results at 35° when the solutions were made up at 50°. The correction factor for solutions made up at 50° and used at 65° is 1.0076.

The coefficient of expansion for distilled water is somewhat

<sup>1</sup> *Loc. cit.*

less than that for an aqueous solution. However, the difference in the coefficients for water and for our most concentrated solution is so small that it is negligible.

By making use of the above correction it was necessary to prepare only one set of solutions for each salt; and, consequently, much pure material and time were saved.

#### *Solubility of Glass.*

The solubility of glass at low temperatures is small, as is well known, but increases rapidly with the temperature and at high temperatures becomes very considerable. At 65° this factor must be taken into account in making conductivity measurements of aqueous solutions in glass vessels.

We reduced this effect to a minimum, and, as we convinced ourselves, to a negligible minimum, in the following way: All of the cells used in this work, as well as all of the bottles for preserving the solutions, were filled with a dilute solution of sodium hydroxide and heated for a number of hours. The glass apparatus was then thoroughly washed out with water. It was next filled with a dilute solution of hydrochloric acid and heated for a long time. The vessels were then carefully washed, filled with distilled water, and heated again. The above process was repeated a number of times.

In this way practically all of the more soluble material on the inner surface of the glass vessels was removed.

We convinced ourselves of this fact by allowing some of our most dilute solutions to stand for a long time, at elevated temperatures, in glass vessels thus treated, and determining the conductivity from time to time. From the slight change in the conductivity we showed that the question of the solubility of the glass was a negligible factor in this work.

Of course, all of the glass vessels used in this work were made of as nonsoluble glass as possible.

#### *Cell Constants.*

Clover and Jones experienced some difficulty in securing reliable cell constants. Results obtained by them seemed to indicate that the cell constants did not remain exactly

constant when the cells were used at different temperatures. When the cells were heated the glass and electrodes expanded and this would produce some change in the constants.

We calculated the magnitude of this change from the longitudinal and cubical expansion of glass, and found that for the conditions under which we worked it was negligible.

The work of Clover and Jones, however, showed that when the cells are heated the change which they undergo persists for a considerable time. The conductivity of a solution was determined at  $35^{\circ}$ . The solution was then heated to  $65^{\circ}$  in the conductivity cell and allowed to remain at that temperature in the cell for about one hour. It was then cooled to  $35^{\circ}$  and the conductivity redetermined after temperature equilibrium had been re-established at this temperature.

In a number of cases the second determination of conductivity at  $35^{\circ}$  differed slightly from the first, showing that the cell constants had undergone a slight change during heating, as we had convinced ourselves that the slight change in conductivity under these conditions was not due to dissolved glass. In all of these cases, however, when the solution, after heating, was allowed to remain in the cell at  $35^{\circ}$  for about three hours, the second conductivity determination always agreed with the first.

This showed that whatever change the cell underwent at the higher temperature disappeared in time when the cell was kept at the lower temperature.

Based upon this fact, we devised and used the following method for determining the cell constants and for making the conductivity measurements, the object being to make the measurements under as nearly as possible the same conditions as were employed in determining the cell constants.

The standard solution of potassium chloride, either 0.02 N or 0.002 N, depending upon the distance apart of the electrode plates, was placed in the conductivity cell. The cell was then heated to  $50^{\circ}$ , and after remaining at that temperature for about an hour was cooled to  $20^{\circ}$ . *As soon as temperature equilibrium* was established at  $20^{\circ}$  the conductivity readings were made and the cell constants calculated.

The same method was employed in determining the conductivity of solutions. The solutions in the cells were first heated to  $50^{\circ}$  and allowed to remain at that temperature for about an hour. The cells were then placed in a bath and cooled down to  $35^{\circ}$ , and as soon as temperature equilibrium was established the conductivity readings were made. The cells were then placed in the  $50^{\circ}$  bath and after the solutions had come to this temperature the conductivity determinations were made. They were then transferred to the  $65^{\circ}$  bath and the corresponding conductivities determined.

We regard this method of determining cell constants and of carrying out conductivity measurements as important. If the cell constant is determined at  $20^{\circ}$  and conductivity measurements made in it at higher temperatures, the calculated constant is not the true constant for the cell. If, on the other hand, the cell is first heated to  $50^{\circ}$ , cooled to  $20^{\circ}$ , and the constant then quickly determined at this temperature we have comparable conditions for determining the constant of the cell and the conductivity of the solutions. The mean of  $35^{\circ}$  and  $65^{\circ}$  is  $50^{\circ}$  and it requires about three hours for the cell to acquire its normal condition at  $20^{\circ}$ . By this method we determine the cell constant after the cell has undergone its temporary small change at the higher temperature.

Experiments similar to those carried out by Clover and Jones, *i. e.*, determining the conductivity of a solution at  $35^{\circ}$ , heating it and then cooling it to  $35^{\circ}$  again and redetermining its conductivity, were carried out. We found practically no change in the conductivity of a solution before and after heating, provided the cell constants had been determined as described above.

Another good reason for warming the solutions in the cells before determining the cell constants and the conductivities of the solutions is to avoid the presence of air bubbles on the electrode plates. By first heating the solutions in the cells to  $50^{\circ}$  and then removing the air bubbles gathered on the plates, no further disturbance due to this change is encountered in determining the conductivities of these solutions at lower temperatures.



The cells when not in use were filled with redistilled water and kept continually in a bath at a temperature of from 45° to 50°. All of the cell constants were redetermined once in about every two weeks. Only very slight changes were found in any of the constants during this entire work.

*Ammonium Bromide.*

The pure salt was heated for several hours in an air bath at 130°. The standardization of the original solution was effected by weighing out the amount of salt necessary to make a 0.25 N solution:

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	139.4	81.29	174.2	78.8	210.6	78.7
8	145.0	84.55	182.2	82.4	220.9	82.5
32	156.2	91.08	196.3	88.8	239.3	89.4
128	163.2	95.16	206.2	93.3	250.9	93.7
512	168.5	98.25	213.7	96.7	259.8	97.0
1024	171.5	100.0	221.0	100.0	267.6	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.32	1.66	2.43	1.39
8	2.48	1.72	2.58	1.42
32	2.67	1.71	2.87	1.46
128	2.87	1.76	2.98	1.45
512	3.01	1.78	3.08	1.44
1024	3.30	1.92	3.11	1.41

*Ammonium Bisulphate.*

The strength of the original solution was obtained by determining the sulphur as barium sulphate.

*Conductivity.*

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
4	248.6	268.0	282.1
16	308.2	334.4	351.3
32	349.7	381.3	403.2
128	435.0	482.3	526.9
512	523.2	603.7	669.4
2048	556.2	656.5	752.7



*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.29	0.52	0.94	0.35
16	1.75	0.57	1.13	0.34
32	2.11	0.60	1.46	0.38
128	3.15	0.72	2.97	0.62
512	5.36	1.02	4.38	0.72
2048	6.68	1.20	6.41	0.97

*Sodium Iodide.*

The original solution was made up by direct weighing. The salt was heated for several days at 150° to constant weight.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	115.9	80.00	146.2	78.2	179.0	76.5
8	121.0	83.5	152.6	81.6	187.5	80.1
32	128.6	88.7	163.4	87.4	200.2	85.5
128	136.2	94.0	173.2	92.6	213.2	91.1
512	142.7	98.5	180.6	96.6	222.0	94.8
1024	144.9	100.0	187.0	100.0	234.1	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond units.	Per cent.	Cond. units.	Per cent.
4	2.02	1.74	2.19	1.49
8	2.11	1.74	2.33	1.52
32	2.32	1.80	2.46	1.50
128	2.47	1.81	2.67	1.54
512	2.53	1.77	2.76	1.53
1024	2.81	1.94	3.14	1.67

*Sodium Carbonate.*

The anhydrous salt was heated for several hours at 130°. The original solution was made up by weighing. As in the case of potassium carbonate, the dissociation was not calculated. The salt is, of course, considerably hydrolyzed, especially at the higher temperatures.

*Conductivity.*

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
4	145.9	190.9	237.9
8	168.5	219.6	271.9
32	209.0	272.1	343.4
128	241.9	318.3	403.3
512	258.0	336.7	424.7
1024	269.7	350.1	439.5

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.00	2.05	3.13	1.64
8	3.41	2.02	3.49	1.59
32	4.21	2.0	4.74	1.74
128	5.09	2.10	5.67	1.78
512	5.25	2.04	5.87	1.74
1024	5.36	1.99	5.96	1.70

*Sodium Acetate.*

The original solution was made up by direct weighing. The sample of salt used was dried in an air bath for several days at 120°.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	75.14	75.5	97.28	74.6	121.0	73.5
8	81.66	82.1	106.0	81.3	131.7	80.1
32	91.10	91.5	117.9	90.4	147.7	89.8
128	97.13	97.6	125.7	96.4	157.5	95.7
512	99.40	99.9	129.3	99.2	162.7	98.9
2048	99.50	100.0	130.4	100.0	164.5	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.47	1.95	1.58	1.62
8	1.62	1.98	1.71	1.61
32	1.79	1.96	1.99	1.69
128	1.90	1.95	2.12	1.69
512	1.99	2.00	2.23	1.72
2048	2.06	2.07	2.27	1.74

## Potassium Iodide.

The sample of salt used was heated in an air bath for several days at a temperature of 120°. The 0.25 N solution was made up by direct weighing.

## Conductivity and Dissociation.

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	139.9	83.5	174.8	80.3	212.7	79.3
8	144.8	86.5	181.5	83.4	221.2	82.5
32	154.0	91.9	194.2	89.2	235.8	87.9
128	160.9	96.1	202.0	92.8	248.0	92.5
512	166.2	99.2	213.3	98.0	261.4	97.5
1024	167.5	100.0	217.6	100.0	268.1	100.0

## Temperature Coefficients.

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.33	1.66	2.53	1.45
8	2.45	1.69	2.65	1.46
32	2.68	1.74	2.77	1.43
128	2.74	1.70	3.07	1.52
512	3.14	1.89	3.22	1.51
1024	3.34	1.99	3.37	1.55

## Potassium Bisulphate.

The sample of salt used was heated in an air bath for several days at 130°.

## Conductivity.

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
4	246.7	265.8	278.9
8	276.0	298.8	313.3
32	353.8	388.4	408.9
128	451.7	502.9	536.7
512	537.4	616.0	675.6
2048	579.7	675.0	747.0

## Temperature Coefficients.

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.27	0.51	0.87	0.33
8	1.52	0.55	0.97	0.32
32	2.31	0.65	1.37	0.35
128	3.41	0.75	2.25	0.45
512	5.24	1.22	3.97	0.64
2048	6.35	1.10	4.80	0.71

*Potassium Carbonate.*

The pure anhydrous salt was dried for some hours at 130° and the mother solution made up by weighing.

*Conductivity.*

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
4	187.9	237.0	288.0
8	199.8	252.1	308.6
32	233.2	297.5	369.9
128	261.7	334.9	422.8
512	278.5	361.0	451.2
1024	285.5	373.3	467.3

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.27	1.74	3.40	1.43
8	3.49	1.75	3.77	1.49
32	4.29	1.79	4.83	1.62
128	4.88	1.86	5.86	1.75
512	5.50	1.97	6.01	1.66
1024	5.85	2.05	6.27	1.69

*Potassium Dichromate.*

The sample of salt used was heated for some hours to constant weight. The 0.25 N solution was made up by direct weighing. The true value of  $\mu_\infty$  is probably reached at a dilution greater than 2048 liters, so our values for  $\alpha$  are, perhaps, only approximations.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	218.0	76.4	272.1	74.3	326.9	72.8
8	233.7	81.9	292.4	79.8	352.9	78.6
32	261.9	91.7	327.3	89.3	396.9	88.4
128	276.3	96.8	346.0	94.4	417.9	93.1
512	279.2	97.8	351.7	96.0	426.8	95.1
2048	285.5	100.0	366.4	100.0	448.9	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.61	1.65	3.65	1.34
8	3.91	1.67	4.03	1.37
32	4.36	1.66	4.64	1.42
128	4.65	1.68	4.79	1.38
512	4.83	1.73	5.01	1.42
2048	5.39	1.88	5.50	1.50

*Potassium Ferrocyanide.*

The original solution was made up by direct weighing.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	334.5	44.5	414.5	44.0	495.6	43.0
8	361.7	48.1	450.6	47.8	543.0	47.1
32	425.6	56.6	535.0	56.8	651.0	56.4
128	521.6	69.3	663.1	70.4	808.3	70.1
512	637.1	84.7	818.7	86.9	1006.3	87.2
2048	723.6	96.2	915.4	97.2	1121.3	97.2
8192	752.4	100.0	941.9	100.0	1153.2	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	5.33	1.59	5.41	1.30
8	5.93	1.64	6.16	1.36
32	7.29	1.71	7.73	1.44
128	9.43	1.81	9.68	1.46
512	12.11	1.90	12.51	1.53
2048	12.79	1.77	13.73	1.50
8192	12.63	1.68	14.08	1.50

*Lithium Bromide.*

The standardization of the original solution was effected by direct weighing. The salt was heated in an air bath for several days at 130°.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	108.0	80.5	137.0	79.0	168.4	77.9
8	109.6	81.7	139.3	80.4	170.4	78.8
32	118.3	88.2	150.7	87.0	186.4	86.3
128	125.5	93.6	160.0	92.3	198.0	91.6
512	132.0	98.4	169.7	97.9	213.6	98.8
2048	134.1	100.0	173.3	100.0	216.1	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.93	1.78	2.09	1.52
8	1.98	1.81	2.07	1.49
32	2.16	1.83	2.38	1.58
128	2.30	1.83	2.53	1.58
512	2.51	1.90	2.93	1.72
2048	2.61	1.94	2.85	1.64

*Lithium Nitrate.*

The salt was heated for several days at 120° to constant weight. The mother solution was made up by direct weighing.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	95.04	76.9	119.6	74.6	146.4	74.0
8	101.7	82.3	128.6	80.2	157.7	79.7
32	108.0	87.4	138.2	86.2	170.1	86.0
128	116.8	94.5	150.1	93.6	184.9	93.5
512	119.7	96.8	154.2	96.2	192.4	97.3
1024	123.6	100.0	160.3	100.0	197.8	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.63	1.71	1.78	1.48
8	1.79	1.76	1.94	1.51
32	2.01	1.86	2.13	1.54
128	2.22	1.90	2.32	1.53
512	2.30	1.92	2.55	1.65
1024	2.45	1.98	2.50	1.56



*Lithium Sulphate.*

The sample of salt used was dried for several days at 150°. The original solution was made up by direct weighing.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	132.8	51.5	168.8	49.8	207.8	48.2
8	154.9	60.0	197.3	58.2	242.7	56.3
32	190.9	74.0	245.7	72.5	301.8	70.0
128	225.2	87.3	290.5	85.7	362.3	84.1
512	247.7	96.0	324.3	95.7	405.0	94.0
1024	256.8	99.5	336.3	99.3	425.5	98.7
2048	258.0	100.0	338.7	100.0	430.8	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.40	1.80	2.60	1.54
8	2.83	1.82	3.00	1.52
32	3.65	1.91	3.74	1.52
128	4.35	1.93	4.78	1.64
512	5.10	2.06	5.38	1.66
1024	5.30	2.06	5.95	1.77
2048	5.38	2.09	6.14	1.81

*Calcium Bromide.*

The exact strength of the original solution was determined by titrating the bromine with a standard solution of silver nitrate.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
8	204.5	67.5	264.2	67.9	328.7	68.1
32	250.0	82.5	316.7	81.5	387.8	80.4
128	273.4	90.2	346.4	89.1	426.5	88.4
512	292.6	96.6	372.4	95.8	461.5	95.7
2048	303.0	100.0	388.6	100.0	482.4	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
8	3.98	1.94	4.30	1.63
32	4.45	1.78	4.74	1.50
128	4.86	1.78	5.34	1.54
512	5.32	1.82	5.94	1.59
2048	5.71	1.88	6.25	1.61

*Calcium Nitrate.*

The strength of the original solution was obtained by direct weighing. The salt was dried in an air bath for several days at 130° to constant weight.

*Conductivity and Dissociation.*

V.	35°.		50°		65°.	
	$\mu_{\eta}$ .	$\alpha$ .	$\mu_{\eta}$ .	$\alpha$ .	$\mu_{\eta}$ .	$\alpha$ .
4	168.2	58.0	212.6	57.2	258.1	56.3
8	187.0	64.5	237.9	64.0	287.8	62.8
32	223.0	76.9	285.6	76.8	350.6	76.5
128	253.3	87.4	323.1	86.9	397.7	86.8
512	276.3	95.3	349.4	94.0	432.5	94.4
2048	289.9	100.0	371.8	100.0	458.3	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.96	1.76	3.03	1.42
8	3.39	1.81	3.33	1.39
32	4.17	1.87	4.33	1.51
128	4.64	1.83	4.97	1.53
512	4.87	1.77	5.54	1.58
2048	5.46	1.89	5.77	1.55

*Calcium Formate.*

The strength of the original solution was obtained by determining the calcium as the sulphate.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	128.5	58.1	161.3	56.3	195.2	54.5
8	150.9	68.2	190.0	66.3	230.8	64.4
32	185.9	84.0	235.5	82.2	287.8	80.3
128	210.2	95.0	268.6	93.7	331.5	92.5
512	220.7	99.7	283.2	98.8	349.6	97.6
2048	221.3	100.0	286.6	100.0	358.2	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.19	1.70	2.26	1.40
8	2.61	1.73	2.72	1.43
32	3.31	1.78	3.49	1.48
128	3.89	1.85	4.13	1.54
512	4.17	1.89	4.43	1.56
2048	4.35	1.96	4.77	1.66

*Strontium Bromide.*

The strength of the mother solution was determined by Mohr's method.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	203.2	64.1	256.3	63.1	312.7	62.4
8	222.8	70.3	282.5	69.6	343.7	68.6
32	250.1	78.9	316.9	78.1	388.7	77.6
128	278.9	87.9	356.2	87.7	437.6	87.3
512	299.1	94.3	380.3	93.7	470.1	93.8
2048	317.1	100.0	405.9	100.0	501.0	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.54	1.74	3.76	1.46
8	3.98	1.78	4.08	1.44
32	4.45	1.78	4.79	1.51
128	5.15	1.84	5.43	1.52
512	5.41	1.81	5.99	1.57
2048	5.92	1.86	6.34	1.56

*Strontium Nitrate.*

The original solution was made up by direct weighing; the salt was heated for several days at 120°.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	162.4	56.1	206.1	55.8	253.7	55.0
8	185.2	63.9	234.3	63.4	288.0	62.5
32	223.9	77.3	284.2	76.9	354.4	76.9
128	253.0	87.4	322.5	87.3	400.7	86.9
512	276.6	95.5	351.7	92.2	441.0	95.7
2048	289.6	100.0	369.3	100.0	460.9	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.91	1.79	3.17	1.54
8	3.27	1.77	3.58	1.53
32	4.02	1.80	4.68	1.65
128	4.63	1.83	5.21	1.62
512	5.01	1.81	5.95	1.69
2048	5.31	1.83	6.11	1.65

*Strontium Acetate.*

The concentration of the mother solution was obtained by determining the strontium as sulphate.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	104.6	48.4	132.4	47.3	160.9	45.4
8	120.9	56.0	153.7	54.9	193.8	54.7
32	162.6	75.3	207.7	74.2	256.5	72.4
128	190.1	88.0	244.3	87.3	305.0	86.1
512	208.2	96.4	267.0	95.4	336.6	95.0
2048	215.9	100.0	279.9	100.0	354.2	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.85	1.77	1.90	1.43
8	2.19	1.81	2.67	1.73
32	3.01	1.85	3.25	1.56
128	3.61	1.90	4.05	1.66
512	3.92	1.88	4.64	1.74
2048	4.27	1.98	4.95	1.77

*Barium Nitrate.*

The specimen of salt used was dried for several days at 130° and then kept in a desiccator until used. The concentration of the mother solution was obtained by weighing.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	150.8	50.9	192.6	51.3	236.5	50.9
8	177.9	60.1	225.3	60.0	274.7	59.2
32	221.9	74.9	281.5	74.9	345.1	74.4
128	256.8	86.7	326.4	86.9	401.8	86.6
512	282.3	95.3	358.6	95.5	443.1	95.4
2048	296.2	100.0	375.5	100.0	464.1	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.78	1.84	2.93	1.52
8	3.16	1.78	3.29	1.46
32	3.97	1.79	4.24	1.51
128	4.64	1.81	5.03	1.54
512	5.08	1.80	5.63	1.57
2048	5.28	1.78	5.91	1.57

*Barium Formate.*

The concentration of the original solution was obtained by determining the barium as sulphate.

*Conductivity.*

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
4	138.6	174.0	209.5
8	157.7	193.7	232.8
32	203.3	257.6	314.9
128	223.1	283.2	344.5
512	235.5	299.1	367.9

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.36	1.70	2.37	1.36
8	2.40	1.52	2.61	1.34
32	3.62	1.78	3.82	1.48
128	4.01	1.80	4.09	1.44
512	4.17	1.77	4.59	1.53

*Barium Acetate.*

The exact strength of the original solution was ascertained by determining the barium as sulphate.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	114.7	51.6	142.8	49.9	172.2	48.2
8	125.5	56.5	156.6	53.5	188.8	52.8
32	173.3	78.0	221.8	77.5	273.5	76.6
128	194.4	87.5	250.7	87.6	311.5	87.2
512	214.7	96.7	276.7	96.7	345.0	96.6
2048	222.1	100.0	286.2	100.0	357.2	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.87	1.63	1.96	1.37
8	2.07	1.65	2.15	1.37
32	3.23	1.86	3.43	1.55
128	3.75	1.93	4.05	1.61
512	4.13	1.92	4.55	1.64
2048	4.27	1.92	4.73	1.65

*Magnesium Bromide.*

The strength of the original solution was determined by titrating a diluted portion of it with a 0.1 N silver nitrate solution. A portion of the original solution was then made exactly 0.25 N and checked by another titration.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	199.1	67.7	251.2	66.6	308.3	65.4
8	208.3	70.8	263.2	69.8	324.4	68.8
32	234.1	79.6	297.6	78.9	367.7	78.0
128	261.1	88.7	332.4	88.2	412.8	87.6
512	279.0	94.8	358.0	95.0	445.5	94.5
2048	294.2	100.0	377.0	100.0	471.3	100.0



*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.47	1.74	3.81	1.52
8	3.66	1.75	4.08	1.55
32	4.23	1.81	4.67	1.57
128	4.75	1.82	5.36	1.61
512	5.27	1.89	5.83	1.63
2048	5.52	1.88	6.25	1.66

*Magnesium Formate.*

The strength of the original solution was obtained by determining the magnesium as the pyrophosphate.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	107.4	48.7	135.7	47.7	164.4	46.7
8	130.6	59.3	165.2	58.1	201.4	57.2
32	166.7	75.7	212.8	74.9	261.8	74.4
128	196.8	89.3	253.8	89.3	313.8	89.1
512	212.0	92.6	273.7	96.3	337.9	96.0
2048	220.3	100.0	284.2	100.0	352.0	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.89	1.76	1.91	1.41
8	2.31	1.77	2.41	1.46
32	3.07	1.84	3.27	1.54
128	3.80	1.93	4.00	1.57
512	4.11	1.94	4.28	1.56
2048	4.26	1.93	4.52	1.59

*Magnesium Acetate.*

The strength of the mother solution was obtained by determining the magnesium as the pyrophosphate.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_{\eta}$ .	$\alpha$ .	$\mu_{\eta}$ .	$\alpha$ .	$\mu_{\eta}$ .	$\alpha$ .
4	87.0	43.7	110.8	42.9	136.1	41.6
8	109.0	54.8	138.8	53.8	171.2	52.3
32	145.2	73.0	187.1	72.4	231.7	70.8
128	171.4	86.2	219.7	85.1	276.6	84.5
512	188.8	94.9	245.9	95.2	310.9	95.0
2048	198.9	100.0	258.2	100.0	327.2	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.59	1.83	1.69	1.52
8	1.99	1.83	2.16	1.56
32	2.79	1.92	2.97	1.59
128	3.22	1.88	3.79	1.72
512	3.81	2.01	4.33	1.76
2048	3.95	1.99	4.60	1.78

*Cadmium Chloride.*

The exact strength of the original solution was obtained by titrating the chlorine with a 0.1 N solution of silver nitrate.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_{\eta}$ .	$\alpha$ .	$\mu_{\eta}$ .	$\alpha$ .	$\mu_{\eta}$ .	$\alpha$ .
4	72.74	26.2	89.9	25.3	106.5	24.2
8	94.54	34.0	117.3	33.0	139.6	31.7
32	143.6	51.7	179.9	50.6	216.2	49.1
128	196.0	70.5	247.1	69.5	300.0	68.1
512	243.6	87.6	309.5	87.1	378.8	86.0
2048	278.0	100.0	355.4	100.0	440.5	100.0

*Temperature Coefficients.*

V.	35°-65°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.14	1.57	1.12	1.25
8	1.52	1.61	1.49	1.27
32	2.42	1.68	2.42	1.34
128	3.41	1.74	3.52	1.42
512	4.39	1.80	4.62	1.49
2048	5.16	1.86	5.67	1.59

*Cadmium Bromide.*

The purified salt was dissolved in conductivity water and the strength of the solution ascertained by determining the bromine as silver bromide.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	64.25	23.5	80.3	22.9	96.4	22.1
8	85.25	31.2	107.0	30.5	128.5	29.5
32	132.4	48.4	167.6	47.8	202.3	46.4
128	183.7	67.1	234.0	66.7	286.4	65.7
512	234.6	85.7	299.1	85.3	369.1	84.6
2048	273.6	100.0	350.7	100.0	436.0	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.07	1.66	1.07	1.33
8	1.45	1.70	1.43	1.34
32	2.35	1.77	2.31	1.38
128	3.35	1.82	3.49	1.49
512	4.30	1.83	4.67	1.56
2048	5.14	1.88	5.69	1.62

*Cadmium Iodide.*

The salt was dried in a desiccator over calcium chloride for a week or more. The original solution was made by direct weighing.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	48.45	18.7	61.70	18.5	74.96	18.1
8	59.94	23.2	77.16	23.1	94.61	22.8
32	100.2	38.8	130.4	39.1	161.3	38.9
128	157.7	61.0	204.8	61.4	254.8	61.4
512	213.3	82.5	276.7	83.0	345.5	83.3
2048	258.5	100.0	333.4	100.0	414.5	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	0.88	1.82	0.88	1.42
8	1.15	1.92	1.16	1.50
32	2.01	2.00	2.06	1.58
128	3.14	1.99	3.33	1.62
512	4.23	1.98	4.59	1.66
2048	4.99	1.93	5.41	1.62

*Zinc Sulphate.*

The mother solution was made up by weighing.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	84.78	28.5	104.6	27.1	122.2	25.6
8	95.66	32.1	117.8	30.6	137.2	28.7
32	128.8	43.3	159.3	41.3	186.9	39.1
128	174.0	58.4	217.9	56.5	259.6	54.4
512	225.1	77.4	286.5	74.3	347.3	72.7
2048	263.8	88.6	338.4	87.8	417.3	87.4
8192	297.8	100.0	385.5	100.0	477.4	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.32	1.56	1.17	1.12
8	1.47	1.54	1.29	1.10
32	2.03	1.58	1.84	1.15
128	2.93	1.68	2.78	1.27
512	4.09	1.82	4.05	1.41
2048	4.97	1.88	5.26	1.55
8192	5.85	1.96	6.13	1.59

*Manganese Chloride.*

The strength of the original solution was obtained by determining the chlorine gravimetrically. By proper dilution a quarter-normal solution was prepared and the other solutions were made from this.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	173.8	59.8	218.0	58.2	263.5	56.6
8	194.1	66.8	245.3	65.5	297.9	63.9
32	226.9	78.1	288.5	77.1	355.0	76.2
128	257.0	88.4	329.0	87.9	406.8	87.3
512	277.9	95.6	357.6	95.5	444.7	95.5
2048	290.7	100.0	374.3	100.0	465.8	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.95	1.69	3.03	1.39
8	3.41	1.75	3.51	1.43
32	4.11	1.81	4.43	1.53
128	4.80	1.87	5.19	1.58
512	5.31	1.91	5.81	1.62
2048	5.57	1.92	6.10	1.63

*Cobalt Chloride.*

The strength of the original solution was ascertained by means of several gravimetric determinations of the chlorine. A portion of the original solution was then made exactly 0.25 N and the other solutions prepared from this by dilution. It is apparent from the tables that the salt is somewhat hydrolyzed in very dilute solutions.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	188.3	66.1	226.4	61.4	274.3	59.2
8	197.6	69.3	249.4	67.6	302.5	65.3
32	227.7	79.9	288.7	78.3	355.6	76.8
128	255.1	89.5	326.7	88.6	404.2	87.3
512	275.5	96.6	352.2	95.5	442.8	95.6
2048	285.1	100.0	368.7	100.0	463.2	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.54	1.35	3.19	1.41
8	3.45	1.74	3.54	1.42
32	4.07	1.79	4.46	1.54
128	4.77	1.87	5.17	1.58
512	5.11	1.86	6.04	1.71
2048	5.57	1.95	6.30	1.71

*Cobalt Bromide.*

The exact strength of the original solution was obtained by determining the bromine as silver bromide. The other solutions were, of course, made by dilution. It is apparent from the tables that the results are of the same general nature as those obtained with the other cobalt salts we have studied.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	189.8	65.7	239.0	64.5	289.6	62.4
8	205.1	71.0	259.4	70.0	315.7	68.0
32	235.6	81.5	299.5	80.8	367.3	79.1
128	258.0	89.3	329.5	88.9	406.7	87.6
512	275.6	95.4	353.1	95.3	436.6	94.0
2048	289.0	100.0	370.6	100.0	464.3	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.28	1.73	3.37	1.41
8	3.60	1.75	3.75	1.44
32	4.26	1.81	4.52	1.51
128	4.77	1.85	5.15	1.56
512	5.17	1.87	5.57	1.58
2048	5.44	1.88	6.25	1.68

*Cobalt Nitrate.*

The strength of the original solution was obtained by determining the cobalt as cobalt sulphate. The other solutions were obtained by dilution. As in the case of cobalt chloride the salt is probably hydrolyzed in dilute solutions.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	172.8	62.2	216.8	61.0	263.5	60.0
8	190.7	68.7	239.7	67.5	291.4	66.4
32	218.5	78.7	276.9	77.9	340.2	77.5
128	244.0	87.9	310.1	87.3	384.0	87.5
512	262.9	94.7	334.7	94.2	414.6	94.4
2048	277.7	100.0	355.3	100.0	439.0	100.0



*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.93	1.69	3.11	1.43
8	3.27	1.71	3.45	1.44
32	3.89	1.78	4.22	1.52
128	4.41	1.81	4.93	1.59
512	4.79	1.82	5.33	1.59
2048	5.17	1.86	5.58	1.57

*Cobalt Acetate.*

The exact strength of the original solution was ascertained by determining the cobalt as sulphate.

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
4	73.2	91.4	110.9
8	86.9	106.8	131.2
32	139.1	175.8	217.1
128	162.0	206.9	256.4
512	187.4	241.9	300.7
2048	200.1	260.4	326.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	1.21	1.65	1.30	1.42
8	1.33	1.53	1.63	1.52
32	2.45	1.76	2.75	1.56
128	2.99	1.84	3.30	1.59
512	3.63	1.94	3.92	1.62
2048	4.02	2.01	4.37	1.68

*Nickel Chloride.*

The concentration of the mother solution was obtained by determining the chlorine, gravimetrically, as silver chloride.

Salts of nickel, like those of cobalt, are probably hydrolyzed to some extent at high dilutions.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
4	174.9	61.1	218.0	59.3	266.0	58.4
8	194.5	67.9	247.3	67.2	301.5	66.2
32	225.5	78.8	288.1	78.3	354.7	77.9
128	251.4	87.8	321.4	87.4	398.4	87.5
512	270.6	94.5	344.4	93.6	426.1	93.5
2048	286.2	100.0	367.9	100.0	455.5	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.87	1.64	3.20	1.46
8	3.52	1.81	3.61	1.46
32	4.17	1.85	4.44	1.54
128	4.66	1.85	5.13	1.59
512	4.92	1.82	5.45	1.58
2048	5.45	1.90	5.84	1.59

*Aluminium Nitrate.*

The strength of the mother solution was ascertained by several gravimetric determinations of the aluminium.

*Conductivity.*

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
32	204.2	260.5	323.0
128	233.2	301.2	381.1
512	265.9	350.8	458.4
2048	296.3	402.2	535.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
32	3.75	1.84	4.16	1.60
128	4.53	1.94	5.33	1.77
512	5.66	2.13	7.17	2.04
2048	7.06	2.38	8.85	2.20

*Aluminium Sulphate.*

After several crystallizations the purified salt was dissolved in conductivity water and the strength of the original solution determined by estimating the aluminium as the oxide.

*Conductivity and Dissociation.*

V.	35°.		50°.		65°.	
	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .	$\mu_v$ .	$\alpha$ .
8	137.2	24.5	167.6	23.1	188.4	20.3
32	197.1	35.2	234.5	32.3	264.6	28.5
128	274.1	49.0	333.3	46.0	387.6	41.7
512	388.1	69.4	483.8	66.7	581.6	62.6
2048	559.3	100.0	725.0	100.0	929.4	100.0

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
8	2.03	1.48	1.39	0.83
32	2.49	1.26	2.01	0.86
128	3.95	1.44	3.62	1.09
512	6.38	1.64	6.52	1.35
2048	11.05	1.98	13.63	1.88

*Chromium Nitrate.*

As in the case of chromium chloride, the strength of the mother solution was obtained by determining the chromium gravimetrically as chromic oxide. Results of the same general character were obtained with chromium nitrate as with the chloride.

*Conductivity.*

V.	$\mu_v$ 35°.	$\mu_v$ 50°.	$\mu_v$ 65°.
4	228.2	289.7	365.2
8	263.0	334.7	419.4
32	321.4	414.8	519.1
128	395.0	517.6	663.2
512	473.2	627.6	809.0
2048	554.3	732.6	937.4

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	4.10	1.80	5.03	1.73
8	4.78	1.82	5.65	1.69
32	6.23	1.94	6.95	1.68
128	8.17	2.07	9.71	1.87
512	10.23	2.18	12.09	1.93
2048	11.88	2.14	13.65	1.86

*Chromium Acetate.*

The concentration of the mother solution was obtained by determining the chromium as the oxide.

*Conductivity.*

V.	$\mu v$ 35°.	$\mu v$ 50°.	$\mu v$ 65°.
4	39.0	49.5	58.5
8	44.5	53.6	65.5
32	55.5	71.1	89.0
128	62.4	81.0	111.3
512	74.4	97.5	135.1
2048	91.8	120.2	169.1

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	0.70	1.79	0.60	1.21
8	0.61	1.37	0.79	1.47
32	1.04	1.87	1.19	1.67
128	1.24	1.99	2.02	2.49
512	1.54	2.07	2.51	2.57
2048	1.89	2.06	3.26	2.71

*Uranyl Chloride.*

The strength of the original solution was determined in the same manner as in the case of uranyl nitrate, the uranium being weighed as the green oxide,  $U_3O_8$ . The salt is, no doubt, considerably hydrolyzed in dilute solution.

*Conductivity.*

V.	$\mu v$ 35°.	$\mu v$ 50°.	$\mu v$ 65°.
4	220.4	274.6	333.2
8	253.5	318.9	387.8
32	301.4	380.3	473.2
128	342.0	439.4	548.5
512	379.4	491.1	610.6
2048	418.5	546.8	693.7

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	3.61	1.64	3.91	1.42
8	4.36	1.72	4.59	1.44
32	5.26	1.74	6.19	1.63
128	6.49	1.90	7.27	1.65
512	7.45	1.96	7.97	1.62
2048	8.55	2.04	9.79	1.79

*Uranyl Nitrate.*

The strength of the original solution was determined by precipitating with ammonia and igniting the precipitate to the green uranoso-uranic oxide,  $U_3O_8$ .

*Conductivity.*

V.	$\mu v$ 35°.	$\mu v$ 50°.	$\mu v$ 65°.
4	176.0	220.1	268.3
8	199.2	251.2	307.1
32	233.8	298.0	372.0
128	275.4	354.6	444.7
512	303.2	395.8	502.0
2048	349.0	460.8	585.3

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
4	2.94	1.67	3.21	1.46
8	3.46	1.74	3.73	1.48
32	4.28	1.83	4.93	1.65
128	5.28	1.92	6.01	1.69
512	6.17	2.03	7.08	1.79
2048	7.45	2.13	8.30	1.80

*Uranyl Sulphate.*

The strength of the original solution was ascertained by determining the uranium as the oxide  $U_3O_8$ . From the original solution the other solutions were prepared by dilution. As in the case of uranyl acetate, the temperature coefficients expressed in percentages decrease with increase in dilution.

*Conductivity.*

V.	$\mu v$ 35°.	$\mu v$ 50°.	$\mu v$ 65°.
16	90.1	110.5	131.3
32	115.9	139.5	162.8
128	155.0	185.0	213.7
512	219.0	264.3	303.7

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
16	1.36	1.51	1.39	1.26
32	1.57	1.35	1.55	1.11
128	2.00	1.29	1.91	1.03
512	3.02	1.38	2.63	0.99

*Uranyl Acetate.*

The strength of the mother solution was obtained by determining the uranium. The temperature coefficients expressed in percentages decrease with increase in dilution. This is rather remarkable, the opposite effect being usually obtained.

*Conductivity.*

V.	$\mu v$ 35°.	$\mu v$ 50°.	$\mu v$ 65°.
16	48.06	59.34	71.36
32	54.92	67.36	80.47
128	72.26	87.65	103.4
512	92.92	111.3	130.0
2048	118.4	141.4	165.4

*Temperature Coefficients.*

V.	35°-50°.		50°-65°.	
	Cond. units.	Per cent.	Cond. units.	Per cent.
16	0.75	1.56	0.80	1.34
32	0.83	1.51	0.87	1.29
128	1.02	1.41	1.05	1.19
512	1.22	1.31	1.25	1.12
2048	1.53	1.29	1.60	1.13

*Discussion of Results.*

That the work done in this laboratory is already of fairly wide scope can be seen from the following statement. The conductivities of the following inorganic compounds have been measured from 0° to 35°:

The bromide, iodide, nitrate, carbonate, diphosphate and acetate of sodium; the chloride, bromide, iodide, nitrate, acid sulphate, sulphate, carbonate, sulphocyanate, chromate, dichromate and ferrocyanide of potassium; the chloride, bromide, nitrate and sulphate of lithium; the chloride and bromide of ammonium; the chloride, bromide and nitrate of calcium; the chloride, bromide and nitrate of strontium; the chloride, bromide, nitrate, formate and acetate of barium; the chloride and sulphate of magnesium; zinc sulphate; the chloride, nitrate, sulphate and acetate of cobalt; the chloride, nitrate, sulphate and acetate of nickel; the chloride and nitrate of



manganese; lead nitrate; the chloride and nitrate of iron; the chloride and nitrate of chromium; the chloride, bromide and nitrate of copper; and hydrochloric, nitric and sulphuric acids.

The conductivities of the following organic acids have been measured from  $0^{\circ}$  to  $35^{\circ}$ : Acetic, propionic, butyric, isobutyric, phenylacetic, mandelic, hippuric, malonic, succinic, maleic, fumaric, crotonic, citraconic, mesaconic, itaconic, racemic, pyrotartaric, citric, pyromucic, benzoic, *o*-toluic, *m*-toluic, *p*-toluic, *o*-phthalic, cinnamic, salicylic, *m*-hydroxybenzoic, *p*-hydroxybenzoic, gallic, *o*-aminobenzoic, *p*-aminobenzoic, metanilic, sulphanilic, oxanilic, benzilic, *p*-nitrobenzoic, *p*-toluenesulphonic,  $\alpha$ -methyaminosulphonic (1,4), *m*-nitrobenzenesulphonic, nitrotoluenesulphonic (4,1,2), trichloroacetic, picric, *o*-nitrobenzoic, *m*-nitrobenzoic and oxalic.

The conductivities of the following compounds, including those recorded in this paper, have been measured from  $35^{\circ}$  to  $65^{\circ}$ :

The bromide, iodide, nitrate, sulphate, carbonate, diphosphate, acetate and tetraborate of sodium; the chloride, bromide, iodide, nitrate, acid sulphate, sulphate, carbonate, diacid phosphate, sulphocyanate, chromate, dichromate, ferrocyanide, acetate, benzoate and aluminium sulphate of potassium; the chloride, bromide, nitrate and sulphate of lithium; the chloride, bromide, nitrate, acid sulphate, sulphate and aluminium sulphate of ammonium; the chloride, bromide, nitrate and formate of calcium; the chloride, bromide, nitrate and acetate of strontium; the chloride, bromide, nitrate, formate and acetate of barium; the chloride, bromide, nitrate, sulphate, formate and acetate of magnesium; zinc sulphate; the chloride, bromide and iodide of cadmium; the chloride, bromide, nitrate, sulphate and acetate of cobalt; the chloride, nitrate and sulphate of nickel; the chloride, nitrate and sulphate of manganese; lead nitrate; the chloride, nitrate and sulphate of aluminium; the chloride, nitrate, sulphate and acetate of chromium; copper sulphate; silver nitrate; and the chloride, nitrate, sulphate and acetate of uranyl.

A study of the data recorded in this paper will show that

relations earlier pointed out<sup>1</sup> for other substances and temperatures hold here also. What these relations are can be seen best by collecting the data in the following tables. The volumes are 4 and 512 and the temperature coefficients are between the temperatures 50° and 65°:

Table I.—Substances with Small Hydrating Power.

	Temperature coefficients in conductivity units.	
	V = 4.	V = 512.
Ammonium bromide	2.43	3.08
Sodium iodide	2.19	2.76
Potassium iodide	2.53	3.21
Lithium bromide	2.09	2.93
Lithium nitrate	1.78	2.55

Table II.—Substances with Large Hydrating Power.

	Temperature coefficients in conductivity units.	
	V = 4.	V = 512.
Calcium bromide	4.22	5.94
Calcium nitrate	4.03	5.54
Strontium bromide	3.76	5.99
Strontium nitrate	3.17	5.95
Barium nitrate	2.93	5.63
Magnesium bromide	3.81	5.83
Manganese chloride	3.03	5.81
Cobalt chloride	3.19	6.04
Cobalt bromide	3.37	5.57
Cobalt nitrate	3.11	5.33
Nickel chloride	3.20	5.45

It has been pointed out that there are several factors which contribute to the increase in the conductivity of solutions of electrolytes with rise in temperature. The diminished viscosity of the solvent with rise in temperature is undoubtedly an important factor in determining the large positive temperature coefficients of conductivity. The *decreasing mass of the ion with rise in temperature* is, however, probably a much more important factor in determining the increase in conductivity as the temperature rises—a suggestion made four years ago and which has been confirmed by all subsequent work. The solvate breaks down, becoming less complex as the temperature rises, and the mass of the moving ion, including the molecules of the solvent combined with the ion proper,

<sup>1</sup> THIS JOURNAL, 35, 445 (1906); 40, 355 (1908); 43, 187 (1910).

becomes smaller with rise in temperature. It will consequently move faster under a constant driving force, and the conductivity will<sup>1</sup> therefore increase as the temperature rises.

The necessary consequences of this conclusion have already been tested at lower temperatures,<sup>2</sup> and for a few substances at temperatures ranging from 35° to 65°.<sup>3</sup> The data for a much larger number of substances are now available, and we can see whether these consequences are borne out by the much larger number of facts.

The conclusions that have been drawn are:

1. Those ions with the greatest hydrating power should have the largest temperature coefficients of conductivity.
2. Substances with equal hydrating power should have approximately the same temperature coefficients of conductivity, or at least temperature coefficients of the same order of magnitude.
3. The temperature coefficients of conductivity for any given substance should be greater the higher the dilution.

The first conclusion is almost self-evident. The more complex the hydrate the greater the change in this complexity with rise in temperature. The greater the change in the mass of the ion the greater the change in its velocity with a constant driving force; consequently, the greater the change in the conductivity with rise in temperature.

A comparison of Table I with Table II will show that the above conclusion is borne out by the facts.

The conclusion that substances with equal hydrating power should have equal temperature coefficients of conductivity would be based upon the assumption that the hydrates formed by different substances would have the same degree of stability with respect to temperature, which is not true. A given ion would hold the combined water more or less firmly than an ion of another metal. We, therefore, should not expect different kinds of ions with approximately the same

<sup>1</sup> THIS JOURNAL, 35, 446 (1906).

<sup>2</sup> *Ibid.*, 43, 187 (1910).

<sup>3</sup> *Ibid.*, 35, 448 (1906); 40, 355 (1908).

hydrating power to have the same temperature coefficients of conductivity. We should, however, expect them to have temperature coefficients of the same order of magnitude. If we compare the results in Table I with one another and then those in Table II with one another, we will see that each set of coefficients is of the same order of magnitude.

The third conclusion is also evident: The greater the dilution the more complex the hydrate formed about the ion. The more complex the hydrate, the greater the change in the complexity with change in temperature. Therefore, the higher the dilution the larger the temperature coefficients of conductivity. If we compare the results for any substance in Table I or Table II at the two dilutions, we will find that at  $V = 512$  the temperature coefficient of conductivity is always larger than at  $V = 4$ .

That the solvates formed by the ions decrease in complexity with rise in temperature is established by a number of lines of evidence. At the boiling points of saturated solutions the hydrates have approximately the composition of the salt with its water of crystallization. The minimum in the boiling-point curves is at a greater concentration than in the freezing-point curves, showing less complex hydrates at the higher temperatures.

The above conclusion is almost self-evidently true. Complexes in general, however great their stability, become simpler the higher the temperature. If the complexes are very stable it often requires a very considerable rise in temperature to produce an appreciable change in composition. But where the complexes are comparatively unstable, as in the case of solvates, a small rise in temperature may produce a very considerable decrease in the complexity of the system.

The necessary consequences of the solvate theory of solution are thus borne out not only qualitatively but quantitatively by the facts recorded in this paper.

The rapid increase in the conductivity of sodium carbonate with increase in dilution is due primarily to the hydrolytic action of the water. The comparatively large temperature coefficients of conductivity are also due to the increase in

hydrolysis with rise in temperature. The same applies to the results with potassium carbonate.

The very high conductivities shown by potassium ferrocyanide, and the large temperature coefficients, expressed in conductivity units, are due to the large number of ions into which this salt dissociates, and to hydrolysis which increases rapidly with dilution and with temperature.

The lithium salts show smaller conductivity than the corresponding sodium, potassium and ammonium salts, due to the fact that the lithium ion is much more strongly hydrated than the other alkali ions, and this produces the well-known slow velocity of the lithium ion.

The large conductivities of salts of the alkaline earths with strong acids are due to the fact that these are strongly dissociated ternary electrolytes, and therefore yield a large number of ions in solution. The large temperature coefficients of conductivity, as has been pointed out, are due to the fact that these ions are strongly hydrated, and the hydrates decrease rapidly in complexity with rise in temperature, thus causing the velocity of the ion to increase rapidly as the temperature is raised. These salts are, of course, somewhat hydrolyzed.

The same comments apply to salts of cobalt and nickel as were made in connection with those of the alkaline earths. Hydrolysis plays an even more prominent part with the former than with the latter compounds.

When we turn to salts of aluminium and chromium we are, of course, dealing with quaternary electrolytes, or molecules that break down into four ions each. The chlorides and nitrates of the metals are also among the most strongly hydrated substances known. Further, these salts are very strongly hydrolyzed. All of these factors taken together explain the rapid increase in conductivity with dilution and the large temperature coefficients of conductivity shown by these compounds.

The conductivities and temperature coefficients of conductivity shown by the uranyl salts are just about what would be expected from the composition and nature of these salts.



Work along the lines indicated in this paper is now being pushed as rapidly as possible in this laboratory. Indeed, five investigators are now at work on the conductivities of aqueous solutions of inorganic and organic compounds at temperatures ranging from  $0^{\circ}$  to  $65^{\circ}$ .

The work is also being extended as rapidly as possible to nonaqueous solvents, and the investigations of the last ten years in this field are being supplemented by several new ones.

PHYSICAL CHEMICAL LABORATORY,  
JOHNS HOPKINS UNIV.,  
June, 1910.

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## REPORT.

### THE INDUSTRIAL FIXATION OF NITROGEN.

An elaboration of a lecture on the industrial fixation of nitrogen, delivered by Professor P. A. Guye, of the University of Geneva, before the French Chemical Society was recently published in the *Bulletin*.<sup>1</sup> In the following pages an attempt is made to abstract those portions of Guye's article which are of special interest or not generally known. The original is a long, detailed history of the subject from the theoretical as well as the technical point of view.<sup>2</sup>

In speaking of the need of nitrogenous fertilizers, the author gives the following figures, quoting in part Caro and H. Erdmann.<sup>3</sup>

#### *Present German Food Supply.*

Crop.	Area in millions of hectares. <sup>4</sup>	Annual crop per hectare in kilos.	Annual crop in millions of metric tons. <sup>5</sup>	Annual importations in millions of tons.
Rye	6.0	1500	9.0	0.57
Wheat	2.4	1880	4.5	2.29
Oats	4.0	1720	6.9	0.97
Potatoes	3.2	12990	41.6	0.35
Barley	1.0	1660	1.7	1.62
Totals	16.6		63.7	5.80

<sup>1</sup> Bull. Soc. Chim., [4] 5, Nos. 20-21.

<sup>2</sup> A report on the oxidation of atmospheric nitrogen covering the theoretical work of Brode and the technical work of Birkeland and Eyde appeared in *THIS JOURNAL* in 1906 (35, 358).

<sup>3</sup> Z. Stickstoff u. Sauerstoff Ind., 1909.

<sup>4</sup> 1 Hectare = 2.5 acres.

<sup>5</sup> 1 Metric ton = 1000 kilograms = 2204 lbs.



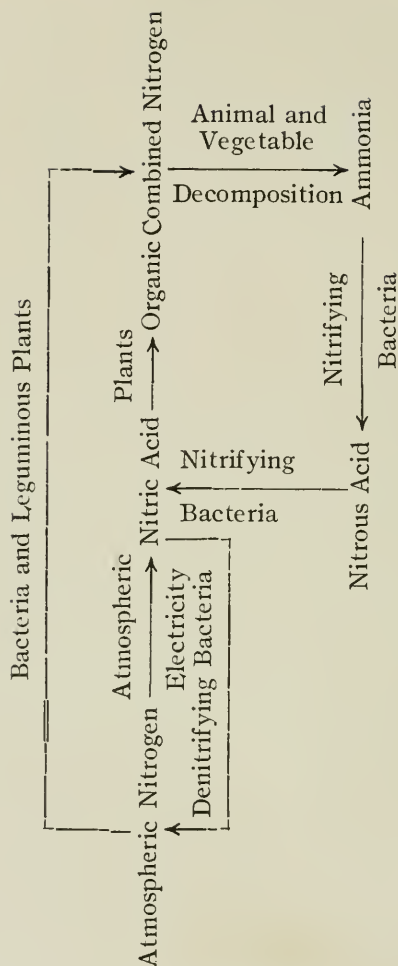
*Increase in German Food Supply through Intensive Cultivation.*

Crop.	Additional nitrogen re- quired per hectare. Kilos.	Increase of crop per kilo nitro- gen per hectare. Kilos.	Increase of crop per hectare in kilos.	Total increase of crop per year in millions of tons.
Rye	60	25	1,500	9.0
Wheat	130	15	2,000	4.8
Oats	100	20	2,000	8.0
Potatoes	120	100	120,000	40.0
Barley	60	25	1,500	1.5
Total,				63.3

These figures show that Germany does not raise food enough to feed its inhabitants, but by intensive cultivation of its soil could feed a much larger population. The figures also show the need of low-priced nitrogen, and indicate a final solution of the problem of cheap bread and cheap food.

Of the fertilizing constituents in chemical fertilizers—potassium, phosphorus and nitrogen—the first two are cheap; but combined nitrogen at Fr. 1.10 to Fr. 1.50 per kilo is too dear for general use. With the drop in price, certain to come in the near future, thorough enriching of the soil will be common, and all harvests will increase enormously in amount, thus causing lower food prices. The nitrogen problem appears in this light as one of the factors of the social question.

If we examine the reserve supply of nitrogen, we find that there are about 7 metric tons of nitrogen in the air over each square meter of the earth's surface, which would suffice for 19,000,000,000 years. Supposing the earth's crust to have an average thickness of 15 kilometers, H. Erdmann considers its nitrogen content as not less than 5 tons per square meter of surface. A small portion of this nitrogen is constantly undergoing change on the earth's surface, taking part in animal and plant life. Through the action of electricity, particularly in polar regions, soluble nitrogen compounds (nitric and nitrous acids and ammonium salts) are formed in the air and fall with the rain on the soil, to be in part reduced by vegetation to free nitrogen which rejoins the air. The following table shows the cycle of nitrogen:



The coal beds and the Chili saltpeter deposits furnish the bulk of the nitrogen used for chemical and agricultural purposes. The nitrogen industry is new. At the beginning of the 19th century the only sources were the saltpeter plantations and animal excrements. The installation of gas works in 1812 and the quite recent processes for recovering the ammonia developed in coking ovens mark the beginning of

industries which at present yield nearly 800,000 tons yearly.<sup>1</sup>

There is a steadily increasing demand for Chili saltpeter. In 1825 935 metric tons were exported; in 1860, 6800; in 1880, 226,000; in 1890, 1,065,000; and in 1908, 2,014,000. The Peruvian government, in 1888, predicted the exhaustion of the deposits in 1913; in 1900, the exhaustion was officially postponed to 1940; and in 1907 again postponed to 2032. These changes are chiefly due to discoveries of new deposits, in part to improved methods of working the old deposits. While the supply is sufficient for the present, the price will rise rather than fall, as the richer deposits are exhausted and the poorer require more labor and fuel per ton of nitrate. Despite the demand, the industry is far from prosperous at present nitrate prices.

When we look to the coal beds for nitrogen, we find that the recent advances in this field are due to the work of Dr. Ludwig Mond, which began in 1879. At that time there were numerous patented processes for obtaining ammonia from air by conducting air mixed with steam over heated porous material, preferably glowing coke. Mond proved that in any one of these processes the amount of ammonia obtained was the same whether air were admitted or not, and that the nitrogen of the ammonia obtained came solely from the coke. Mond's own process consists in making generator gas at as low temperatures as possible, thus avoiding certain decompositions and obtaining most of the nitrogen in the coal as ammonia. About two tons of water per ton of coal are mingled with air and introduced into the generator. The resulting gas contains 60-70 per cent. of the nitrogen of the coal in the form of ammonia, which is absorbed by sulphuric acid; the gas is used as fuel under the name of "Mond gas." The best method of using this or any other generator gas is to burn it in gas engines.

Within the last few years the Mond system has been successfully applied to poor lignite and wet peat. Poor lignite deposits and peat bogs are yielding ammonium sulphate and electrical energy.<sup>2</sup>

Methods for the production of synthetic ammonia by the action of electric discharges on a mixture of nitrogen and

<sup>1</sup> H. Erdmann estimates the production of ammonium sulphate for 1907 at 778,400 metric tons, of which Great Britain produced 310,000, Germany 260,000, and the United States only 60,000, despite the fact that 40,770,000 tons of coke were made in the United States in 1907.

<sup>2</sup> Frank and Caro say of their adaptation of the Mond process to wet peat that the electrical energy (from dynamos driven by gas engines burning the Mond gas) is clear profit, as the ammonium sulphate pays working expenses and interest on capital.

hydrogen, or by decomposition of metallic nitrides, with subsequent regeneration of the nitride, are not as yet of commercial value. The electric discharge tends to decompose the ammonia at temperatures below that of formation, and similar difficulties are encountered with the nitrides. The author thinks that it is probable that the hindrances to these methods may be overcome. The raw material is at hand. Hydrogen may at need be extracted from water gas; it is obtained as unused by-product in the electrolytic production of sodium hydroxide; the hydrogen now wasted would, however, yield only 39,000 tons of ammonium sulphate yearly. Nitrogen may be obtained at relatively low price by fractioning liquid air, for—even considering the oxygen as dead loss—the nitrogen costs only 0.2 to 1 cent per kilo. As a kilo of ammoniacal nitrogen is worth 40 cents, and as it is of great advantage to the nitric acid industry to work with air very rich in oxygen, we shall see in the future processes such as the synthetic preparation of ammonia or cyanamide worked by the side of processes for synthetic nitric acid.

There are two successful methods of transforming ammonia into nitric acid. The first is by lowering the oxidation temperature of the ammonia by suitable catalyzers, completing the oxidation at temperatures below that at which ammonia decomposes. A German establishment by this method obtains from coking-oven ammonia two tons of 88 per cent. nitric acid per 100 tons of coal. The second method of oxidation is that of Professor Muntz, in Paris, who utilizes the bacteria of peat bogs for this purpose. The oxidizing power of these bacteria seems to be so enormous that if synthetic ammonia could be obtained in sufficient quantity at low price we should have a complete solution of the nitrogen problem.

Calcium cyanamide is made by the well-known process of Frank and Caro, which consists in fixing nitrogen by calcium carbide, thus converting it into the cyanamide,  $\text{CaCN}_2$ , and is so well known that it is only necessary to recall the advantage of combining its manufacture with that of nitric acid, using the excess nitrogen for the first and equal volumes of nitrogen and oxygen for the second.

In all processes for oxidizing atmospheric nitrogen by electrical energy the action is really thermal. Air is acted on by the heat generated by the electric arc in special furnaces; some of the atmospheric nitrogen combines with some of the oxygen of the air, forming nitric oxide, which, after leaving the furnace, is converted by atmospheric oxygen into

nitrogen dioxide; to transform the nitrogen dioxide into salable products, the air containing these nitrous vapors is submitted to various processes, the simplest of which is the action of water or of bases, yielding nitric acid or a mixture of nitrate and nitrite.

That the electric spark brings about the formation of oxides of nitrogen in the air was shown by Priestley in 1785 and by Cavendish in 1788. Perrot, in 1861, obtained the same results with the Ruhmkorff coil (mixture of sparks and small arcs) and was the first to show that prolonged discharges produce a greater amount of nitric acid than short discharges. Berthelot, in 1870, showed that the electric arc produces the same chemical effects as the spark, but with greater intensity. As the work of Rayleigh, of Dougal and Howles, of Kowalski and Moscicki, the earlier work of Guye and Naville, and the processes of Bradley and Lovejoy and Birkeland and Eyde were so fully described in *THIS JOURNAL*,<sup>1</sup> Guye's descriptions may be omitted.

In studying the three types of furnace in actual use, we see that in the Birkeland-Eyde system a moving arc is employed, the magnetic field acting as motive force. In the processes of the Badische Aniline and Soda Company and of Guye a quiet arc is used. Guye thinks that at the working temperatures ( $2500^{\circ}$ – $4000^{\circ}$ ) of the great arc furnaces, the speed of the gaseous molecules is so great, and their mixture by diffusion so rapid, that it is practically superfluous to hasten the mixing process by the sweeping action of the moving arc. The one essential condition is that the interior of the oxidation chamber shall be practically filled by the arc.

The Badische Company's furnace, as described by Schönherr,<sup>2</sup> has a practically motionless arc in the axis of the long,

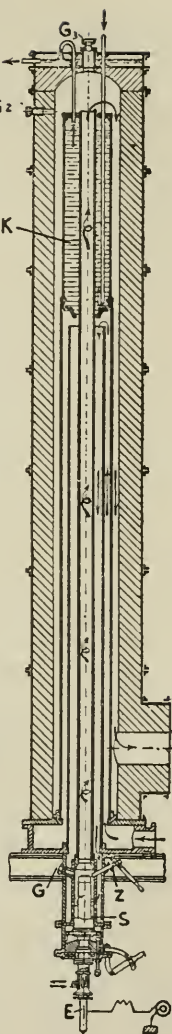


Fig. 1.

<sup>1</sup> *THIS JOURNAL*, 35, 358. To make the present article clear, it may be said that the principle of the Birkeland furnace is to force a rapid current of air across a flame disc at high temperature, causing the oxidation of a part of the nitrogen. The flame disc in a 500 kilowatt furnace is two meters in diameter and is formed by the action of the magnetic field on the arc. The yield from a furnace of this size is 500 kilos nitric acid per 10-hour day.

<sup>2</sup> *Electrotech. Z.*, 1909, Nos. 16, 17. *Witt: Chem. Ind.*, 28, 609.



narrow, vertical oxidation chamber. The essentials of this furnace (Fig. I) are a central metallic tube, the upper part of which is cooled by water circulation, and a lower electrode, *E*, also cooled by water. The points of attachment of the arc are the head of the electrode *E* and the upper water-cooled part of the furnace. The top of the arc can be observed through the openings  $G_2$  and  $G_3$ , the lower part through the opening *G*. The circulation of the air is shown by the arrows. By passing twice around the central tube, the air is heated to  $500^\circ$ , and enters the tube at the base through an opening placed tangentially to the axis. According to Schö-

nherr, this causes a rotating movement of the air in the central tube, the arc being the motionless axis of this air spiral; and the length and stability of the arc depend upon the rotary motion of the air.<sup>1</sup>

Schönherr claims as advantages of the Badische Company's furnace, as compared with the Birkeland furnace, greater simplicity and economy, as it does not require the fragile and costly apparatus for forming a magnetic field. The arc—which for a 600 h. p. (442 kilowatts) furnace is 5 meters long—glows quietly in the axis of the furnace and requires little care; it is rarely extinguished and is easy to re-establish. The yield is said to be better than that of

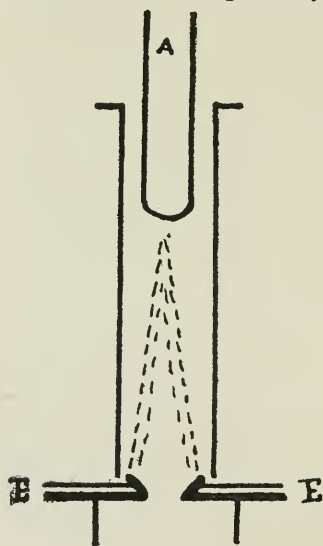


Fig. II.

the Birkeland furnace.

Guye then describes his own furnace. He uses an arc playing between two electrodes at the base of a vertical tube; air enters the tube at the base. The upward draught in the tube elongates the arc into the form of an inverted V, as shown in Fig. II. Guye's furnace is shown diagrammatically in Fig.

<sup>1</sup> Guye says that his experiments show that the arc remains nearly as constant in the center of the tube if the air enters freely the lower open end of a vertical tube, the tube forming one electrode, a terminal below the lower opening the other. In this case rotation is impossible. He ascribes the great stability of these arcs to the fact that gas viscosity increases with the temperature; for nitrogen, at  $-191^\circ$   $\eta = 0.324$ ; at  $+300^\circ$ ,  $\eta = 1.6279$ ; that is, in an interval of  $500^\circ$ , the ratio of increase in viscosity is 1:5.



III. Five vertical tubular chimneys,  $C, C,$  stand in a chamber, into which air enters through the openings  $O, O$ . The air may be heated by circulating about the tubes. The electrodes  $E$  are in electric tension. The stability of this system of several arcs is much greater than that of a single arc of the same tension, each arc serving as autoregulator to its neighbor. The sum of the lengths of the arcs is much greater for a given current than in any other furnace. In his furnace of 50 kilowatts power working at a tension of 5,000 volts

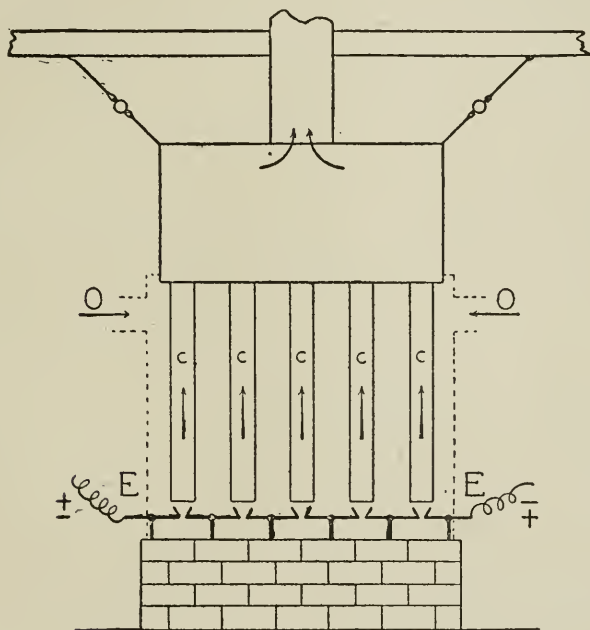


Fig. III.

with 5 arcs, the sum of the length of the arcs is between 5 and 6 meters. The Badische Company's 442 kilowatt furnace working at 4,200 volts with nearly nine times the power produces an arc of five meters in length.

The tubular chimneys are narrow enough to be completely filled by the arc. A cooler may be put above the arc  $A$  (Fig. II) to ensure more rapid cooling of the gases, at the moment of their leaving the zone of oxidation, without cooling the electrodes. A little experimental furnace of this kind ran day and night for 6,000 hours; for some months it ran every

night without attendance. The 50 kilowatt furnace has been running at Geneva for over half a year with satisfactory results; in the roughly constructed furnace without preliminary heating of air and without cooling apparatus, the yield is 545 to 560 kilos nitric acid per kilowatt year. The 2 kilowatt experimental furnace yielded 350-390 kilos per kilowatt year. This increase of yield with increase of power conforms to theory and leads Guye to expect a much higher yield in his new 500 kilowatt furnaces now in course of construction at Geneva.

In the processes now in use, only 3 per cent. of the total energy employed is utilized in the oxidation of nitrogen. Improvements suggested by the author are as follows:

1. The use of dried air. Nitrate of lime would probably be the best drying agent, as it is readily dehydrated again by waste heat.
2. Compression of the nitrous vapor before entering the absorption apparatus.
3. The partly de-oxygenated air leaving the absorption apparatus should not be allowed to re-enter the furnace.
4. A mixture of air and oxygen should be substituted for air.
5. Work under reduced pressure (about 100 mm.) in the oxidation chamber increases yield.

By adopting some of the features enumerated the author thinks the yield can be increased to 1000 kilos per kilowatt year.

In all of these processes for making nitric acid, the gases on leaving the furnace are utilized to heat steam boilers. The temperature of the gases entering the boiler tubes is about 700°; that of the gas leaving the tubes about 250°-300°. At these temperatures the tubes are scarcely injured by the gases, which then pass into the re-oxidation tower, cooling tower, and finally enter the absorption apparatus at temperatures below 100°. The absorbing agents are water or sulphuric acid or basic solutions.

When air traverses a furnace and absorbs the following stages may be distinguished:

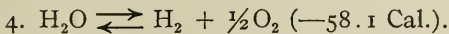
*Stage a.* Air is rapidly heated to 3000° or higher. Above 1500° nitric oxide, NO, is formed.

1.  $\frac{1}{2}\text{N}_2 + \frac{1}{2}\text{O}_2 \rightleftharpoons \text{NO}$  ( $-21.6$  Cal.).
2.  $\text{N} + \text{O} \rightleftharpoons \text{NO}$  (? Cal.).

When the air contains moisture—ordinary air always does—it is possible that a small quantity of nitric oxide is formed by the following reaction:



At the same time most of the water vapor dissociates.



The free hydrogen and oxygen could react in two opposite ways, either lessening the content of nitric oxide through the reducing action of the hydrogen, or increasing it through the increase in oxygen concentration. The author's experiments show that increase of water vapor in the air means a decrease in production of nitric oxide and lead him to consider the reducing effect predominant.

*Stage b.* The first cooling from the temperature of the arc to about  $1200^\circ$  causes the reversion of nitric oxide to nitrogen and oxygen if the cooling is not instantaneous; this reversion is never entirely avoided.

*Stage c.* The second period of cooling extends from  $1000^\circ$  to  $500^\circ$ – $600^\circ$ . Apparently no important chemical transformations occur in this stage.

*Stage d.* The third period of cooling begins at  $500^\circ$ – $600^\circ$  and reaches to ordinary temperatures. It is marked by the different oxidation equilibria of nitric oxide into the oxides, which may occur in different ways; either by successive oxidation:  $\text{NO} \rightarrow \text{N}_2\text{O}_3 \rightarrow \text{NO}_2 \rightarrow \text{N}_2\text{O}_4$  (Berthelot, Raschig); or by a direct oxidation:  $\text{NO} \rightarrow \text{NO}_2$  with ulterior formation of  $\text{N}_2\text{O}_3$  by addition of NO to  $\text{NO}_2$  (Lunge, Engler). The first view is generally accepted; probably both are correct and both reactions simultaneous. Whatever the interpretation, the important fact is that with air containing 1–2 per cent. of nitric oxide, at ordinary temperatures, a final equilibrium results between the gases present; this certainly occurs between nitric oxide and nitrogen peroxide, probably nitrogen trioxide is also in the mixture. The presence of the oxide  $\text{N}_2\text{O}_4$  is admitted by all workers; that of nitric oxide and nitrogen peroxide the author has proved by isolating these gases. The relative proportions of the oxides  $\text{NO}_2$ ,  $\text{N}_2\text{O}_4$ ,  $\text{N}_2\text{O}_3$  and NO will vary with the concentration of combined nitrogen. In dilutions of about 1 per cent. oxides of nitrogen, the free nitric oxide forms 10–20 per cent. of these oxides; 0.9 of the remainder is nitrogen peroxide,  $\text{NO}_2$ , and 0.1 is the oxide  $\text{N}_2\text{O}_4$  with a little trioxide.

The dilution of the oxides of nitrogen in practical work, and their equilibrium, explain the great difficulty found in ab-

sorbing these oxides completely by water or even by sulphuric acid.

In the cooled furnace gases, nitrogen peroxide predominates; a small part is present as  $N_2O_4$ , which reacts with alkali or water, a fresh quantity forming from the peroxide  $NO_2$ . The reaction with water is: (a)  $N_2O_4 + H_2O = NO_3H + NO_2H$ ; (b)  $3NO_2H = NO_3H + H_2O + 2NO$ . As the nitric oxide formed in reaction (b) is re-oxidized, all oxides would be finally changed to nitric acid were it not for the conditions of equilibrium referred to above; and further, as the concentration of the unabsorbed oxides diminishes a point is reached where the oxide  $N_2O_4$  becomes unstable and dissociates into the peroxide  $NO_2$ . From this point the further absorption is in the form of nitrous acid. (c)  $NO_2 + NO + H_2O = 2NO_2H$ , or (d)  $N_2O_3 + H_2O = 2NO_2H$ . This nitrous acid then decomposes according to reaction (b). It can be calculated that if the absorption follows the cycle  $a-b$ , the gases must run through this cycle four times to absorb 99 per cent. of the oxides of nitrogen; but if it follows the cycle  $c-b$  or  $d-b$ , it must run through nine times to reach the same result.

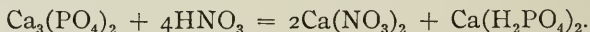
These last considerations show why if an absorption by water is followed by an absorption by alkali the yield from the alkali absorption is principally nitrite. It is true, however, that some of the nitrite is formed by the reaction discovered by Gay-Lussac and studied by Sabatier:  $4NO + 2NaOH = N_2O + 2NaNO_2 + H_2O$ .

Industrially 40 per cent. nitric acid is obtainable by water absorption, even from very dilute gases.

If nitrite is desired it is better to conduct the furnace gases over alkali while still at a temperature of  $300^\circ$ . This is the principle of the Badische Company's nitrite process.

The concentration of the acid is best carried out by using calcium nitrate as dehydrating agent; two successive treatments with this brings the 40 per cent. acid to 95 per cent. without loss of nitrous fumes.

Coignet has patented a process to substitute nitric for sulphuric acid in the manufacture of superphosphate:



By conducting the furnace gases over calcium phosphate, the salts  $Ca(NO_3)_2$ ,  $Ca(NO_2)_2$  and  $Ca(H_2PO_4)_2$  are formed. This mixture would be an excellent fertilizer.

It has been proposed to isolate the oxide  $N_2O_4$  by cooling

the furnace gases to low temperatures; considering the great dilution, it would be necessary to cool the whole mass of gas to  $-100^{\circ}$  to separate all the compound  $N_2O_4$ . Sir William Ramsay has patented a process for combining this cooling with the liquefaction of air and separation of oxygen from nitrogen, his purpose being to treat a mixture of equal volumes of the two gases in the oxidation furnace.

Guye has shown experimentally that the impure oxide  $N_2O_4$  can be purified by passing oxygen through it, and that its transformation into the oxide  $N_2O_3$ , by adding nitric oxide, takes place smoothly. Further, the dried liquids,  $N_2O_3$  and  $N_2O_4$ , do not act on metal containers. Hence the industrial transportation and use of these liquefied gases presents no more difficulty than that of chlorine or phosgene.

If the oxide  $N_2O_4$  could be marketed at low price, it might effect a revolution in the manufacture of explosives, as mixtures of it with various organic compounds yield high-power explosives which, as yet, have been little studied.

We all know that it is necessary, in changing alkali chlorides to nitrates, to evaporate repeatedly with nitric acid in excess, and that the escaping gases are a mixture of unchanged hydrochloric acid, of chlorine and of oxides of nitrogen. Therefore, there is as yet no industrial production of sodium nitrate by this reaction. Guye says that he will soon publish details of a method by which a quantitative yield of hydrochloric acid and sodium nitrate can be obtained by this reaction. So synthetic Chili saltpeter may yet be brought on the market. Calcium chloride may be changed to calcium nitrate by the same method, thus closing the last gap in the cycle of the Solvay process by marketing the worthless calcium chloride as calcium nitrate and hydrochloric acid.

Methods of employing the energy wasted in the furnace processes will doubtless be developed in the future. At present a furnace absorbing 1000 kilowatts energy and producing 500 tons nitric acid yearly, develops during the same period as much heat energy as is developed by burning 1000 tons of coal, while according to Schönherr only 30 per cent. of this energy is utilized in making steam;<sup>1</sup> yet this 30 per cent. is equivalent to 300 tons of coal for each 500 tons of acid.

E. RENOUF.

<sup>1</sup> Schönherr says of the Badische Company's furnace, that 3 per cent. of the energy is used in forming nitric acid, 40 per cent. is absorbed in cooling the gases before entering the boilers, 17 per cent. is lost by radiation, 30 per cent. is recovered by the boilers, and 10 per cent. is lost by the cooling after the gases leave the boilers.

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## OBITUARIES.

GEORGE FREDERICK BARKER.

George Frederick Barker, a past president of the American Chemical Society and of the American Association for the Advancement of Science, was born in Charlestown, Massachusetts, July 14, 1835, and died at Philadelphia, May 10, 1910. His early education was obtained in the public schools of Boston and at the academy of South Berwick, Maine. He next served an apprenticeship with Joseph Wightman, a well-known maker of scientific instruments in Boston, from whom he received a mechanical training which served him in good stead in later years. The ability to construct his own apparatus was gained in those early days. With this preparation he entered the Sheffield Scientific School, from which he graduated in 1858 as Bachelor of Philosophy. From 1859 to 1861 he was an assistant in the Harvard Medical School, then Professor of Chemistry in Wheaton College, Illinois, and afterwards in the Albany Medical College, which gave him his degree of M.D. In 1863 he taught in the University of Pittsburgh, and in 1868 and 1869 he delivered lectures on chemistry in Williams College. In 1869 he was appointed Professor of Physiological Chemistry and Toxicology in the Yale Medical School, going thence, in 1872, to the chair of Physics in the University of Pennsylvania, where the remainder of his scientific career was spent. In 1900 he was made Emeritus Professor, but that did not imply any cessation of his real activity. His contributions to science continued till within a few years of his death.

In his scientific work Professor Barker was peculiarly versatile. On the one hand he was intensely interested in purely theoretical questions, as may be seen from the most casual inspection of his text-book on "Elementary Chemistry." He often gave to American audiences their first hearing of new advances in theoretical chemistry, and in doing so he displayed to a remarkable degree the gift of clearness. On the other hand, much of his attention was devoted to technical subjects, the application of science to human welfare. As a court expert he was much in demand, and was most successful. Theory and practice, to him, went hand in hand as inseparable partners. His keen critical faculty was a source of strength to him in both fields of his activity.

In strictly original investigation, Professor Barker's output was not large. In his younger days, problems of organic and



physiological chemistry occupied much of his attention. Later, as Professor of Physics, his mind turned more to electrical questions. His adaptability to widely dissimilar conditions is thus clearly shown. In which field of work he appeared to the best advantage it would be difficult to say. During the later years of his life he was much interested in radioactivity, and studied especially the radioactivity of thorium minerals,

Apart from his duties as a teacher, Professor Barker found time for other occupations. For some years he served on the Board of Education of Philadelphia. He was in charge of the spectroscopic work of an expedition made to observe the total solar eclipse of 1878. In 1881 he was United States Commissioner to the Electrical Exhibition at Paris, and vice-president of the Jury of Awards. In recognition of this service, France made him a "Commander" in the Legion of Honor. He also served as juror at the Chicago Exposition of 1893.

Professor Barker was president of the American Association for the Advancement of Science in 1879, and of the American Chemical Society in 1891. He was also a member of the National Academy of Sciences, an officer of the American Philosophical Society, a corresponding member of the British Association, and honorary member of the Royal Institution. Honorary degrees were given him by the University of Pennsylvania, Allegheny College, and McGill University.

On the social side, Professor Barker was a delightful companion. He enjoyed attending scientific gatherings, and meeting his coworkers in the advancement of knowledge. There was nothing of the pedant or recluse in his character. His presence will be much missed in the various organizations to which he belonged.

F. W. CLARKE.

#### HEINRICH CARO.

Hofrath Dr. Heinrich Caro, known to chemists as the former scientific head of the Badische Anilin- und Soda-Fabrik, died Sept. 11th, aged 76.

Caro was born in Posen in 1834. He studied in the Posen Gymnasium and in the University and Gewerbe-Schule of Berlin; in the latter institution he was a pupil of the young Professor Adolph von Baeyer. Caro became interested in color chemistry and devoted himself to technical work first in Mühlheim in 1855, then in Manchester in 1859, where he was in the employ of Roberts, Dale & Co., subsequently becoming a member of the firm. Two German chemists of high at-

tainment in color chemistry were then residing in England, A. W. Hofmann and Peter Gries; Caro was in touch with them and with W. H. Perkin, and the friendship and influence of these three men were a spur to the talented young chemist. A new method for making mauveine, the discovery of the alcohol-soluble blue indulines, and the Manchester yellow patented by Dale, Martius and himself, were among the results of his stay in England. In 1866 he returned to Germany, going to Heidelberg and intending to devote himself to pure chemistry. In 1868, however, he was offered the position of technical manager and head chemist of the Badische Anilin- und Soda-Fabrik; he accepted this position and remained in active service with this company until 1890, and was connected with it in an advisory capacity till the time of his death. The constant and rapid development of this firm from its comparatively small importance at its start to the vast field of industry covered by its present activity is largely due—perhaps chiefly due—to Caro's ability in chemical research and his remarkable power of guiding and inspiring each and every one of his host of young coworkers in carrying out their several investigations. Space is lacking to mention the discoveries in new dyestuffs made by Caro with the help of the constantly growing army of young chemists—all picked men, mostly university graduates with the doctor's degree—who are in the employ of this great establishment. Caro's lecture before the German Chemical Society, in 1891, published in the *Berichte* of that year, gives an idea of their number and importance.

In addition to Caro's grasping and controlling the chemical work of the factory he found time for purely scientific investigations. Witness his papers with Graebe and Liebermann on synthetic alizarin, with Graebe on rosolic acid, rosaniline and acridine, with Baeyer on oxyanthraquinones, nitroso-diphenylaniline and nitrosophenol.

Caro took a leading part in the improvement of the patent laws in Germany and in most of the prominent movements for the encouragement and regulation of chemical industry.

On Caro's retirement from active participation in the work of the factory in 1890, he did not cease his chemical work but continued it in his own laboratory; perhaps the most striking result of the work of this period was his discovery of the "Sulfo-monopersauere," better known as Caro's acid.

Caro's personality was attractive; he was quiet and reserved, much beloved by his friends, coworkers and all who had the privilege of knowing him.

E. R.

## ZDENKO HANS SKRAUP.

Prof. Zdenko Hans Skraup, known to all chemists for his work on the quinic alkaloids and for the synthesis of quinoline which bears his name, died suddenly on Sept. 10th.

Prof. Skraup was born in Prague on March 3, 1850. His early education was received in the schools of his native city and in 1871, after one year's military service, he became assistant to Prof. H. L. Buff in the Prague Technical High School, from which he had just graduated. Shortly after he took up technical work and for a time was employed in a porcelain and stoneware factory and later in the Vienna mint. In 1873, however, following his bent for scientific research, he accepted an assistantship in the University of Vienna under Prof. Rochleder, at whose suggestion he began a study of the oxidation of cinchonine, his first step on a road he was to follow so long and with so much success. After Rochleder's death, in 1874, Skraup remained with his successor, Lieben, and for a time his work on the alkaloids was interrupted. In 1875 he obtained his doctor's degree at Giessen. While with Lieben, he studied the iron-cyanogen compounds, but soon resumed his investigations of cinchonine and related compounds, and although again called to the field in 1878 with the army of occupation in Bosnia, where he so distinguished himself that he was given a decoration and promoted to a first lieutenancy, he was able, within the next 15 years, to shed much light on this problem, and his work has contributed largely towards establishing the constitution of the quinic alkaloids. It was during this period that he discovered his famous quinoline synthesis (1880).

In 1881 he became professor of chemistry at the Vienna "Handelsakademie." Six years later he succeeded Maly at the Technical High School in Graz and the following year he accepted a professorship at the university in the same city, which he held until 1906, when finally, on a second call, he went to the University of Vienna. While in Graz he continued his investigations on the alkaloids, but his activity was by no means limited to this field, as is shown by his work on maleic and fumaric acids, the discovery of the formation of a new biose in the hydrolysis of cellulose, the preparation of lead tetrachloride, and the extensive study of albumens which he began in 1904.

Skraup was a member of many scientific societies and vice-president of the Deutsche Chemische Gesellschaft. He was cut off in the fulness of his activity, and by his death chemistry suffers an inestimable loss.

## REVIEWS.

THE SIMPLE CARBOHYDRATES AND THE GLUCOSIDES. By E. FRANKLAND ARMSTRONG, D.Sc., Ph.D., Associate of the City and Guilds of London Institute. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1910. pp. ix + 112.

This treatise is one of the series of "Monographs on Biochemistry" edited by R. H. Aders Plimmer and F. G. Hopkins. It is highly recommended to chemists interested in carbohydrates and enzymes. There are seven chapters dealing with the pentoses, hexoses, disaccharides, the relation between configuration and properties, hydrolysis and synthesis, and the natural and synthetical glucosides. The bibliography is very full. The book does not give a complete account of the sugars, but furnishes rather a summary of the more recent advances to those already familiar with the carbohydrates.

The treatment of the relation between configuration and enzyme action is excellent, much of Armstrong's own work in this field helping to illuminate the subject. There are some loose statements: On page 9 it is stated that "when glucose is prepared by artificial means, a mixture in equal proportions of *d*- and *l*-forms is actually obtained." The author surely does not stop to think that *d*-glucose is made *artificially* from *d*-mannose or *d*-fructose without the simultaneous production of *l*-glucose. In some other similar cases, however, the actual facts are clear from the context.

This book and that of Bayliss on "The Nature of Enzyme Action" together give an excellent account of some of the actions of amylolytic and proteolytic enzymes.

S. F. ACREE.

DIE SPRENGSTOFFE, IHRE CHEMIE UND TECHNOLOGIE. VON DR. RUDOLF BIEDERMANN, Geheimer Reg.-Rat und Professor der Chemie an der Universität Berlin. 286 Bändchen. Aus Natur und Geisteswelt, Sammlung wissenschaftlich-gemeinverständlicher Darstellungen. Mit 15 Figuren im Text. Leipzig: Druck und Verlag von B. G. Teubner. 1909. pp. iv + 128. Price, M. 1.25.

This work, like its companions in the "Aus Natur und Geisteswelt" series, is in the convenient form of a pocket edition and it demonstrates that, through the careful selection of material, the exercise of a sound sense of proportion, and the use of concise but clear methods of expression, a large amount of valuable information may be compressed into a small space and yet be in a convenient form for use. The subject matter is divided into three chapters: The historical development of the invention of explosives, the theory of explosives, and the technology of explosives. Under the sec-



ond chapter there are presented in sufficient detail to serve as a useful introduction for beginners or as a reminder to those skilled in the art, the subjects of the energy of explosives, their thermochemistry, comparative efficiency, reaction equations, gaseous volumes, velocity of decomposition, initial impulse, explosion temperatures, explosion pressures, and density of loading. In the third chapter is given a sufficient number of typical examples of explosives to illustrate all the various classes. The book contains several illustrations, a large number of tables of data, and frequent references to literature. It is brought up to the date of publication and is sound and trustworthy.

CHARLES E. MUNROE.

THE MECHANICAL APPLIANCES OF THE CHEMICAL AND METALLURGICAL INDUSTRIES. A Complete Description of the Machines and Apparatus used in Chemical and Metallurgical Processes for Chemists, Metallurgists, Engineers, Manufacturers, Superintendents and Students. By OSKAR NAGEL, PH.D., Consulting Chemical Engineer. With 292 Illustrations. Second Edition. New York: Published by the Author, P. O. Box 385. 1909. pp. vii + 307.

This book, following on somewhat similar lines the well-known work of Parnicke, is intended, according to the author's statement in the preface, "to clear up ideas regarding the mechanical appliances used in the chemical and metallurgical industries, to expose the real importance of the machines used in the various processes and to get rid of the obscurities prevailing at present in these matters." The reader of the book soon experiences a feeling that the author has not entirely succeeded in all his aims. Many of the machines and appliances are accorded very meagre treatment, while the frequent omission of index letters or numbers from the diagrams and text render the descriptions far from clear; as, for example, the inadequate consideration of the topics of Magnetic Separation, of Steam Pumps, of Crushing Rolls and Jaw Crushers. Even the excellent diagram of the Positive Pressure Blower, Fig. 120, hardly warrants dismissing the subject with the statement: "The working of this machine is so simple and so well known that a detailed description is not necessary." Probably most engineers and superintendents would understand the working of this machine from the diagram alone, but nontechnically trained chemists, manufacturers and students may not. Complicated diagrams, such as Figs. 43 and 97, without index lettering, are of little service in elucidating the text. Throughout the book there is considerable verbiage and repetition.

But overlooking these defects, there really is much useful

information for the nontechnical reader, and the engineer may find something here and there in the work. The chapters on Steam and Water, Electric Power, Gas Power, Purification of Gases, Firing and Furnaces, Drying Appliances and Separating, are well done. A short chapter on Temperature Measurements closes the book proper; in the appendix is a paper by the late Mr. Oscar Guttman on "The Works Chemist as Engineer," read before the Society of Chemical Industry. The mechanical make-up of the book is very good; the type is very legible and the illustrations are generally clear and sharp. A few misprints have crept in, notably on p. 36 (time for tank), p. 42 (retort for retard), and p. 153 (sulphuric for sulphurous).

F. H. THORP.

THEORETICAL PRINCIPLES OF THE METHODS OF ANALYTICAL CHEMISTRY BASED UPON CHEMICAL REACTIONS. By M. G. CHESNEAU, Ingenieur en Chef des Mines, Professeur d'Analyse Minérale à l'École National des Mines. Authorized translation by AZARIAH THOMAS LINCOLN, Ph.D., Assistant Professor of Chemistry, Rensselaer Polytechnic Institute, and DAVID HOBART CARNAHAM, Ph.D., Associate Professor of Romance Languages, University of Illinois. New York: The Macmillan Co. 1910. pp. x + 184. Price, \$1.75.

The author has classified and discussed theoretically a number of analytical operations in an interesting way, and has made rather free use of mathematical formulas in his treatment of the subject. Perhaps the most novel feature of the work is the use of a "calorimetric" method of explaining the phenomena of solutions, instead of the employment of the ionic theory as a basis. To the reviewer, the method adopted seems far less satisfactory than the one which Ostwald has made so well known in a book upon the same subject. However, the author of the present work devotes a chapter to the electrolytic theory of double decomposition of salts, and another chapter to objections to the theory, so that fully one-quarter of the book is devoted to a discussion of the view which he has not adopted. These chapters may be useful to those who are interested in the controversial aspect of the ionic theory.

Although one of the translators is a professor of Romance Languages, it appears that a slip has been made here and there in the rendering of the French into English. For instance, on page 172, sulphuric and oxalic acids are designated as being *rare*, whereas the evident intention is to say that they are *exceptional* in a certain behavior. The book has the inconvenient lack of an alphabetical index, as is frequently the case with books of French origin.

H. L. WELLS.



DIE BESTIMMUNGSMETHODEN DES WISMUTS und seine Trennung von den anderen Elementen. Von PRIVATDOZENT DR. L. MOSER, Technische Hochschule Wien. Die Chemische Analyse. Sammlung von Einzeldarstellungen auf dem Gebiete der chemischen, technisch-chemischen und physikalisch-chemischen Analyse. Herausgegeben von DR. B. M. MARGOSCHES, Privatdozent an der Deutschen Technischen Hochschule, Brünn. Stuttgart: Verlag von Ferdinand Enke. 1909. pp. 126. Price, M. 4.

The purpose of this book, as outlined in the preface, is to present as complete an account as possible of the analytical chemistry of bismuth, and to collect information which may be of value in future research in this field. Many analytical processes are accordingly described which are of historical or chemical interest, but which are of little value in accurate analytical work. For this reason, however, and on account of the author's successful treatment of the subject, the book will undoubtedly have a wider circle of readers than would a mere description of a few reliable methods of analysis.

In the introduction of fifteen pages the author considers briefly the general chemistry of bismuth, including its history, occurrence, and preparation from the ores. Qualitative tests and separations are dealt with in ten pages; and the remainder of the book is devoted to quantitative methods of analysis under the following heads: (I) gravimetric, 18 pp.; (II) volumetric, 11 pp.; (III) colometric, 1 p.; (IV) gasometric, 1 p.; (V) electroanalytical, 9 pp.; (VI) separations, 25 pp.; and (VII) analysis of special substances, 16 pp.

The last section of the book will prove of especial value to the practical analyst, since it deals with the problems most frequently encountered in actual work, *viz.*, analyses of the crude metal, ores, alloys, and pharmaceutical products. The usefulness of the book is also increased by the fact that the author's experience in this field has enabled him to judge of the value of many of the methods. He considers the gravimetric determination of bismuth as phosphate to be the best method of analysis and points out the sources of error in many other methods.

W. C. BRAY.

POST'S CHEMISCH-TECHNISCHE ANALYSE. Zweiter Band. Viertes Heft. Dritte vermehrte und verbesserte Auflage, herausgegeben von PROF. DR. BERNHARDT NEUMANN, Grossherzogliche Technische Hochschule Darmstadt. Mit zahlreich eingedruckten Abbildungen. Braunschweig: Vieweg und Sohn. 1909. pp. xiv + 467. Price, M. 12.

This part of the latest edition of Post's well-known handbook of the methods of chemico-technical analysis is devoted to coal tar, the mineral pigments, the natural and synthetic dyestuffs, and the color lakes. Except for a few paragraphs carried over from the edition of 1890, these chapters have

been entirely rewritten with the addition of so much new matter that the number of printed pages is increased about fourfold. The fact that the work of compilation was entrusted to the hands of Professor Gustav Schultz, of Munich, is in itself a guarantee that the material used has been judiciously selected and arranged. The volume will be found a valuable work of reference by all who are interested in the manufacture, use, or analysis of colors. S. P. MULLIKEN.

**TOXIKOLOGISCHE CHEMIE.** Von DR. E. MANNHEIM. Privatdozent für pharmazeutische Chemie an der Universität Bonn. Mit 6 Abbildungen. Sammlung Göschen. No. 465. Leipzig: G. I. Göschen'sche Verlagsbuchhandlung. pp. 150. Price, M. o. 80.

A booklet of 150 pages, representing one of a series of very elementary writings on the various branches of chemical science published under the name of "Sammlung Göschen." Being written very clearly it answers the purpose of acquainting the reader with the fundamental principles of practical Toxicology. As a book of reference or for any detailed study it is naturally not suitable. C. V.

**AUSFÜHRLICHES LEHRBUCH DER PHARMAZEUTISCHEN CHEMIE.** Bearbeitet von DR. ERNST SCHMIDT, Geh. Regierungsrat, o. Professor der pharmazeutisch-chemischen Instituts der Universität Marburg. Mit 95 eingedruckten Abbildungen. Zweiter Band. Organische Chemie. Fünfte vermehrte Auflage. Erste Abtheilung. Braunschweig: Druck und Verlag von Friedrich Vieweg und Sohn. 1910. S. xvi + 1020. Preis, geheftet, M. 23; geb., M. 25.50.

The author in this part of his extensive work on Pharmaceutical Chemistry considers those chemical substances of the aliphatic series that are important to the pharmacist. In the introduction we find a well-outlined discussion of the relationship of the various groups of organic compounds in regard to constitution and properties. Analytical methods are described in detail. The customary classification of organic chemistry is adopted. Illustrations of chemical apparatus are freely inserted. For those chemicals used in Pharmacy the Latin names of the Pharmacopea are adopted beside the purely chemical nomenclature. The occurrence in nature of the organic substances and their isolation and preparation are well described. The book is up-to-date and thoroughly scientific. One objection may be raised in regard to the absence of references to the more important original papers. This represents one, although perhaps the only, deficiency of this system. C. V.

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(4) Phenylmethanecarboxylic acid (phenylacetic acid). <i>Dakin</i> .....	47
Na (p. 161). <i>White and Jones</i> .....	168
$C_8H_{12}O_5$ . Diethyl ester of $\beta$ -hydroxyethene- $\alpha,\alpha$ -dicarboxylic acid (diethyl hydroxymethylenemalonate). <i>Reynolds</i> .....	314
$C_8H_{16}O_2$ . Heptane- $\alpha$ -carboxylic acid (caprylic acid). <i>Dakin</i> ...	46

## 8 III.

$C_8H_5O_2I_3$ . 2,4,6-Triiodophenyl ester of methanecarboxylic acid. <i>Raiford and Heyl</i> .....	212
$C_8H_7O_4N$ . 2-Nitro-3-methylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	122, 507
$C_8H_8O_3N_2$ . Amide of 2-nitro-3-methylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	123, 507



$C_8H_9O_2N$ . 2-Amino-3-methylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	123, 507
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## 8 IV.

$C_8H_8O_2NI$ . (1) 4-Iod-2-methylaminobenzene-1-carboxylic acid. <i>Wheeler and Johns</i> .....	450
(2) 5-Iod-2-amino-3-methylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	124, 507

C<sub>9</sub>-GROUP.

## 9 II.

$C_9H_8O_2$ . $\beta$ -Phenylethene- $\alpha$ -carboxylic acid (cinnamic acid). Na (p. 161). <i>White and Jones</i> .....	188
$C_9H_{10}O_2$ . 3,5-Dimethylbenzene-1-carboxylic acid (mesitylenic acid). <i>Wheeler and Hoffman</i> .....	117
$C_9H_{10}O_4$ . Ethyl ester of furane-2-[ $\alpha$ -ketoethane- $\beta$ -carboxylic acid] (furoylacetic ester). Na, K (p. 407). Cu (p. 408). <i>Torrey and Zanetti</i> .....	405
$C_9H_{18}O_2$ . Octane- $\alpha$ -carboxylic acid (nonylic acid). <i>Dakin</i> .....	46

## 9 III.

$C_9H_7OCl$ . Chloride of $\beta$ -phenylethene- $\alpha$ -carboxylic acid (cinnamyl chloride). <i>Kohler, Heritage and Burnley</i> .....	64
$C_9H_8O_2N_2$ . 5-Keto-1-[ $\alpha$ -ketoethyl]-3-[2-furyl]-4,5-dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	413
$C_9H_8O_5N_2$ . 2-Nitro-4-acetaminobenzene-1-carboxylic acid. <i>Wheeler and Johns</i> .....	446
$C_9H_9O_3N$ . Benaminomethanecarboxylic acid (hippuric acid). Na (p. 161). <i>White and Jones</i> .....	170
$C_9H_9O_4N$ . (1) 2-Nitro-3,5-dimethylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	118
(2) 4-Nitro-3,5-dimethylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	118
$C_9H_9O_5N$ . Ethyl ester of furane-2-[ $\beta$ -oximido- $\alpha$ -ketoethane- $\beta$ -carboxylic acid] (isonitrosofuroylacetic ester). <i>Torrey and Zanetti</i> .....	410
$C_9H_{10}O_4N_2$ . (1) Ethyl ester of 4-nitro-2-aminobenzene-1-carboxylic acid. <i>Wheeler and Johns</i> .....	444
(2) Ethyl ester of 2-nitro-4-aminobenzene-1-carboxylic acid. <i>Wheeler and Johns</i> .....	448
$C_9H_{11}OBr$ . 2-Brom-3-keto-1-phenyl-2,3-dihydroindene. <i>Kohler, Heritage and Burnley</i> .....	72
$C_9H_{11}O_2N$ . (1) 2-Amino-3,5-dimethylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	119
(2) 4-Amino-3,5-dimethylbenzene-1-carboxylic acid. <i>Wheeler and Hoffman</i> .....	119

- $C_9H_{11}O_4N$ . Ethyl ester of furane-2-[ $\alpha$ -oximidoethane- $\beta$ -carboxylic acid] (oxime of furoylacetic ester). *Torrey and Zanetti*. . . . . 408

## 9 IV.

- $C_9H_7OCIBr_2$ . Chloride of  $\alpha,\beta$ -dibrom- $\beta$ -phenylethane- $\alpha$ -carboxylic acid. *Kohler, Heritage and Burnley*. . . . . 69
- $C_9H_8ONi_3$ . (1) 2,4,6 - Triiod - 3 - acetamino - 1 - methylbenzene. *Wheeler and Hoffman*. . . . . 133
- (2) 4,5,6-Triiod-3-acetamino-1-methylbenzene. *Wheeler and Hoffman*. . . . . 505
- $C_9H_8O_2ClBr$ . Acid from  $\alpha,\beta$ -dibrom- $\beta$ -phenylpropionic acid and  $AlCl_3$ . *Kohler, Heritage and Burnley*. . . . . 71
- $C_9H_8O_3NI$ . 6-Iod-3-acetaminobenzene-1-carboxylic acid. *Wheeler and Hoffman*. . . . . 130
- $C_9H_9ONi_2$ . (1) 2,5-Diiod-3-acetamino-1-methylbenzene. *Wheeler and Brautlecht*. . . . . 498
- (2) 2,6-Diiod-3-acetamino-1-methylbenzene. *Wheeler and Brautlecht*. . . . . 134
- (3) 4,5-Diiod-3-acetamino-1-methylbenzene. *Wheeler and Scholes*. . . . . 143
- (4) 4,6-Diiod-3-acetamino-1-methylbenzene. *Wheeler and Hoffman*. . . . . 132
- (5) 5,6-Diiod-3-acetamino-1-methylbenzene. *Wheeler and Hoffman*. . . . . 504
- $C_9H_9O_2Ni_2$ . Ethyl ester of 4,5-diiod-2-aminobenzene-1-carboxylic acid. *Wheeler and Johns*. . . . . 452
- $C_9H_{10}ONI$ . 4 - Iod - 3 - acetamino - 1 - methylbenzene. *Wheeler and Scholes*. . . . . 140
- $C_9H_{10}O_2NI$ . 4 - Iod - 2 - ethylaminobenzene - 1 - carboxylic acid. *Wheeler and Johns*. . . . . 449

 $C_{10}$ -GROUP.

## 10 II.

- $C_{10}H_{10}O$ .  $\gamma$ -Keto- $\alpha$ -phenyl- $\alpha$ -butene (benzalacetone). *Getman*. . . . . 154
- $C_{10}H_{10}O_2$ .  $\alpha$ -Hydroxy- $\delta$ -keto- $\delta$ -phenyl- $\alpha$ -butene (formylethyl-phenyl ketone). *Reynolds*. . . . . 312, 316
- $C_{10}H_{12}O_2$ .  $\gamma$ -Phenylpropane- $\alpha$ -carboxylic acid. *Dakin*. . . . . 48
- $C_{10}H_{16}O_5$ . Diethyl ester of  $\beta$ -ethoxyethene- $\alpha,\alpha$ -dicarboxylic acid (diethyl ethoxymethylenemalonate). *Reynolds*. . . . . 320
- $C_{10}H_{20}O_2$ . Nonane- $\alpha$ -carboxylic acid (capric acid). *Dakin*. . . . . 46

## 10 III.

- $C_{10}H_{10}O_3N_2$ . (1) *l* - 2,4 - Diketo - 5 - [4 - hydroxyphenylmethyl] - tetrahydro - 1,3 - diazole (*l* - *p* - hydroxybenzylhydantoin). *Dakin*. . . . . 55
- (2) *i* - 2,4 - Diketo - 5 - [4 - hydroxyphenylmethyl]tetrahydro - 1,3-diazole. *Dakin*. . . . . 56

- $C_{10}H_{13}O_2N$ . 2-Ethylamino-3-methylbenzene-1-carboxylic acid.  
*Wheeler and Hoffman*. . . . . 123, 507
- $C_{10}H_{13}O_4N_2$ . Ethyl ester of furane-2-[ $\alpha$ -semicarbazinoethane- $\beta$ -carboxylic acid] (semicarbazone of furoylacetic ester). *Torrey and Zanetti*. . . . . 410

## 10 IV.

- $C_{10}H_{10}O_2NCl$ . (1) 2-Keto-4-chlormethyl-3-phenyltetrahydrooxazole. *Johnson and Langley*. . . . . 359
- (2) 2-Keto-5-chlormethyl-3-phenyltetrahydrooxazole. *Johnson and Langley*. . . . . 357
- $C_{10}H_{11}O_2NCl_2$ . (1)  $\beta,\gamma$ -Dichloropropyl ester of phenylaminoformic acid. *Johnson and Langley*. . . . . 360
- (2)  $\beta$ -Chlor- $\alpha$ -chlormethylethyl ester of phenylaminoformic acid. *Johnson and Langley*. . . . . 357
- $C_{10}H_{11}O_2NBr_2$ . (1)  $\beta,\gamma$ -Dibromopropyl ester of phenylaminoformic acid. *Johnson and Langley*. . . . . 360
- (2)  $\beta$ -Brom- $\alpha$ -brommethylethyl ester of phenylaminoformic acid. *Johnson and Langley*. . . . . 360
- $C_{10}H_{12}O_2NI$ . Ethyl ester of 5-iod-2-amino-3-methylbenzene-1-carboxylic acid. *Wheeler and Hoffman*. . . . . 125, 507

## 10 V.

- $C_{10}H_{11}O_2NClBr$ . (1)  $\gamma$ -Chlor- $\beta$ -brompropyl ester of phenylaminoformic acid. *Johnson and Langley*. . . . . 359
- (2)  $\beta$ -Chlor- $\gamma$ -brompropyl ester of phenylaminoformic acid. *Johnson and Langley*. . . . . 358
- (3)  $\beta$ -Brom- $\alpha$ -chlormethylethyl ester of phenylaminoformic acid. *Johnson and Langley*. . . . . 358

**C<sub>11</sub>-GROUP.**

## 11 II.

- $C_{11}H_{12}O$ .  $\gamma$ -Keto- $\alpha$ -phenyl- $\alpha$ -pentene (benzalmethylethyl ketone). *Getman*. . . . . 155
- $C_{11}H_{14}O_2$ . (1)  $\alpha$ -Keto- $\gamma$ -ethoxy- $\alpha$ -phenylpropane ( $\beta$ -ethoxypropiophenone). *Reynolds*. . . . . 321
- (2)  $\beta$ -Phenylbutane- $\alpha$ -carboxylic acid (ethylphenylpropionic acid). *Reynolds*. . . . . 316

## 11 III.

- $C_{11}H_{10}O_4N_2$ . 3-Keto-1,2-di-[ $\alpha$ -ketoethyl]-5-[2-furyl]-2,3-dihydro-1,2-diazole (1,2-diacetyl-1-furyl-5-pyrazolone) *Torrey and Zanetti*. . . . . 413
- $C_{11}H_{15}O_2N$ . (1) Ethyl ester of 4-amino-3,5-dimethylbenzene-1-carboxylic acid. *Wheeler and Hoffman*. . . . . 120
- (2) 2-Ethylamino-3,5-dimethylbenzene-1-carboxylic acid. *Wheeler and Hoffman*. . . . . 122
- $C_{11}H_{15}O_2N_2$ .  $\beta$ -[4-Nitrophenylhydrazone]pentane. *Dakin*. . . . . 46

## II IV.

$C_{11}H_{11}O_2NCl_2$ . (1) $\beta,\gamma$ -Dichloropropyl ester of benzaminoformic acid. <i>Johnson and Guest</i> .....	465
(2) $\beta$ -Chlor- $\alpha$ -chlormethylethyl ester of benzaminoformic acid. <i>Johnson and Guest</i> .....	460
$C_{11}H_{11}O_2NBr_2$ . (1) $\beta,\gamma$ -Dibromopropyl ester of benzaminoformic acid. <i>Johnson and Guest</i> .....	466
(2) $\beta$ -Brom- $\alpha$ -brommethylethyl ester of benzaminoformic acid. <i>Johnson and Guest</i> .....	465

## II V.

$C_{11}H_{11}O_2NCIBr$ . (1) $\gamma$ -Chlor- $\beta$ -brompropyl ester of benzaminoformic acid. <i>Johnson and Guest</i> .....	466
(2) $\beta$ -Chlor- $\gamma$ -brompropyl ester of benzaminoformic acid. <i>Johnson and Guest</i> .....	466
(3) $\beta$ -Brom- $\alpha$ -chlormethylethyl ester of benzaminoformic acid. <i>Johnson and Guest</i> .....	465

**C<sub>11</sub>-GROUP.**

## 12 II.

$C_{12}H_{12}O_2$ . $\alpha$ -Phenyl- $\alpha,\gamma$ -pentadiene- $\delta$ -carboxylic acid ( $\alpha$ -methylcinnamylidenacetic acid). <i>Macleod</i> .....	338
$C_{12}H_{14}O_4$ . $\beta$ -Phenylbutane- $\alpha,\alpha$ -dicarboxylic acid. + $H_2O$ . <i>Reynolds</i> .....	315
$C_{12}H_{22}O_4$ . Diethyl ester of $\beta$ -ethylbutane- $\alpha,\alpha$ -dicarboxylic acid (diethyl diethylmethylmalonate). <i>Reynolds</i> .....	321
$C_{12}H_{24}O_2$ . Undecane- $\alpha$ -carboxylic acid (lauric acid). <i>Dakin</i> ....	47

## 12 III.

$C_{12}H_9O_2N$ . $\alpha$ -Cyan- $\delta$ -phenyl- $\alpha,\gamma$ -butadiene- $\alpha$ -carboxylic acid ( $\alpha$ -cyanocinnamylidenacetic acid). <i>Macleod</i> .....	347
$C_{12}H_{14}OBr_2$ . $\beta,\gamma$ -Dibrom- $\alpha$ -keto- $\beta$ -methyl- $\alpha$ -phenylpentane (propylidenethylphenyl ketone dibromide). <i>Reynolds</i> .....	317
$C_{12}H_{17}O_2N$ . 2-Diethylamino-3-methylbenzoic acid. <i>Wheeler and Hoffman</i> .....	124, 507

## 12 IV.

$C_{12}H_{11}O_4N_2Cl$ . Benzamide of 2-keto-5-chlormethyltetrahydrooxazole-1-carboxylic acid. <i>Johnson and Guest</i> .....	462
$C_{12}H_{11}O_2NBr_2$ . Diacetate of 2,6(?)-dibrom-4(?)-acetamino-1,3-dihydroxybenzene. <i>Raiford and Heyl</i> .....	218
$C_{12}H_{16}O_2NI$ . 5 - Iod - 2 - diethylamino - 3 - methylbenzene - 1 - carboxylic acid. <i>Wheeler and Hoffman</i> .....	125, 507

**C<sub>13</sub>-GROUP.**

## 13 II.

$C_{13}H_{14}O_2$ . Methyl ester of $\alpha$ -phenyl- $\alpha,\gamma$ -pentadiene- $\delta$ -carboxylic acid (methyl $\delta$ -methylcinnamylidenacetate). <i>Macleod</i> .....	340
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$C_{13}H_{16}O$ . $\gamma$ -Keto- $\delta$ , $\delta$ -dimethyl- $\alpha$ -phenyl- $\alpha$ -pentene (benzalpinacolin). <i>Getman</i> .....	155
$C_{13}H_{20}O_2$ . $\gamma$ -Hydroxy- $\alpha$ -ethoxy- $\gamma$ -phenylpentane (ethylethoxy-ethylphenylcarbinol). <i>Reynolds</i> .....	322

## 13 III.

$C_{13}H_9O_3N_2$ . 4 - Oximido - 5 - keto - 1 - phenyl - 3 - [2 - furyl] - 4,5 - dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	419
$C_{13}H_9O_4N_2$ . 5 - Keto - 1 - [4 - nitrophenyl] - 3 - [2 - furyl] - 4,5 - dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	429
$C_{13}H_{10}O_2N_2$ . (1) 3 - Keto - 1 - phenyl - 5 - [2 - furyl] - 2,3 - dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	429
(2) 5 - Keto - 1 - phenyl - 3 - [2 - furyl] - 4,5 - dihydro - 1,2 - diazole. HCl (p. 416). <i>Torrey and Zanetti</i> .....	416
$C_{13}H_{10}O_2N_2$ . 4 - Phenylazo - 5 - keto - 3 - [2 - furyl] - 4,5 - dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	415
$C_{13}H_{14}O_2Br_2$ . Methyl ester of ? - dibrom - $\alpha$ - phenyl - ? - pen - tene- $\delta$ -carboxylic acid. <i>Macleod</i> .....	346
$C_{13}H_{14}O_2Br_4$ . Methyl ester of $\alpha$ -phenyl- $\alpha$ , $\beta$ , $\gamma$ , $\delta$ -tetrabromopentane- $\delta$ -carboxylic acid. <i>Macleod</i> .....	346
$C_{13}H_{17}ON$ . Amide of $\beta$ -ethyl- $\delta$ -phenyl- $\gamma$ -butene- $\alpha$ -carboxylic acid. <i>Macleod</i> .....	349
$C_{13}H_{19}O_2N$ . 2 - Diethylamino - 3,5 - dimethylbenzene - 1 - car - boxylic acid. <i>Wheeler and Hoffman</i> .....	122

## 13 IV.

$C_{13}H_9O_2N_2Br$ . 5 - Keto - 1 - [4 - bromphenyl] - 3 - [2 - furyl] - 4,5 - dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	427
$C_{13}H_{10}O_3N_2S$ . 5 - Keto - 3 - [2 - furyl] - 4,5 - dihydro - 1,2 - diazole - 1 - [benzene-4-sulphonic acid]. + $H_2O$ . <i>Torrey and Zanetti</i> ..	428

 $C_{14}$ -CROUP.

## 14 II.

$C_{14}H_{28}O_2$ . Tridecane- $\alpha$ -carboxylic acid (myristic acid). <i>Dakin</i> ..	47
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## 14 III.

$C_{14}H_{10}O_2N_2$ . 5-Keto - 4 - benzylidene - 3 - [2 - furyl] - 4,5 - dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	414
$C_{14}H_{11}O_3N_2$ . (1) Phenylamide of 5-keto-3-[2-furyl]-4,5-dihydro-1,2-diazole-1-carboxylic acid (furylpyrazolonephenylurea). <i>Torrey and Zanetti</i> .....	414
(2) 4-Nitroso-3-keto-1-methyl-2-phenyl-3-[2-furyl]-2,3-dihydro-1,2-diazole. HCl (p. 427). <i>Torrey and Zanetti</i> .....	425
$C_{14}H_{12}O_2N_2$ . 3 - Keto - 1 - methyl - 2 - phenyl - 5 - [2 - furyl] - 2,3 - dihydro-1,2-diazole. HCl (p. 423, 425). HBr (p. 424). HI (p. 422). Picrate (p. 424). <i>Torrey and Zanetti</i> .....	422, 425

- $C_{14}H_{13}O_2N$ . Ethyl ester of  $\alpha$ -cyan- $\delta$ -phenyl- $\alpha,\gamma$ -butadiene- $\alpha$ -carboxylic acid (ethyl  $\alpha$ -cyancinnamylidenacetate). *Macleod*.. 347  
 $C_{14}H_{17}O_3N$ . Monamide of  $\beta$ -ethyl- $\delta$ -phenyl- $\gamma$ -butene- $\alpha,\alpha$ -dicarboxylic acid. K (p. 348). *Macleod*..... 349

## 14 IV.

- $C_{14}H_{11}ON_3S$ . 5 - Mercapto - 1,4 - diphenyl - 4,5 - dihydro - 1,2,4 - triazole - 3,5 - oxide (5 - thiol - 1,4 - diphenylurazole). *Nirdlinger* and *Acree*..... 219  
 $C_{14}H_{13}N_2IS$ .  $\alpha$  - [4 - Iod - 1 - methylphenyl] -  $\beta$  - phenylthiourea. *Wheeler* and *Scholes*..... 140

**C<sub>15</sub>-GROUP.**

## 15 II.

- $C_{15}H_{13}N_2$ . 3,5-Diphenyl-1,2-diazole. *Reynolds*..... 324

## 15 III.

- $C_{15}H_{10}OBr_2$ . (1) 2,6-Dibrom-3-keto-1-phenyl-2,3-dihydroindene. *Kohler, Heritage* and *Burnley*..... 75  
 (2) Stereoisomer (?) of 2,6-dibrom-3-keto-1-phenyl-2,3-dihydroindene. *Kohler, Heritage* and *Burnley*..... 75  
 $C_{15}H_{11}OBr$ . (1)  $\alpha$  - Keto -  $\alpha$  - [4 - bromphenyl] -  $\gamma$  - phenyl -  $\beta$  - propene (benzal-*p*-bromacetophenone). *Kohler, Heritage* and *Burnley*..... 66  
 (2) 6-Brom-3-keto-1-phenyl-2,3-dihydroindene. *Kohler, Heritage* and *Burnley*..... 67  
 $C_{15}H_{12}O_3N_2$ . 3 - Keto - 1 - [ $\alpha$ -ketoethyl] - 2 - phenyl - 5 - [2-furyl] - 2,3-dihydro-1,2-diazole. *Torrey* and *Zanetti*..... 417

**C<sub>16</sub>-GROUP.**

## 16 II.

- $C_{16}H_{22}O_4$ . Diethyl ester of  $\beta$ -phenylbutane- $\alpha,\alpha$ -dicarboxylic acid. *Reynolds*..... 315  
 $C_{16}H_{32}O_2$ . Pentadecane- $\alpha$ -carboxylic acid (palmitic acid). *Dakin*. 47

## 16 III.

- $C_{16}H_{13}ON_3$ . 1-Semicarbazone-3-phenylindene. *Kohler, Heritage* and *Burnley*..... 73  
 $C_{16}H_{15}O_5N$ . Ethyl ester of furane-2-[ $\gamma$ -phenylamino- $\alpha,\gamma$ -diketopropane- $\beta$ -carboxylic acid] (anilide of furoylmalonic ester). *Torrey* and *Zanetti*..... 411  
 $C_{16}H_{19}O_2N$ . Ethyl ester of  $\alpha$ -cyan- $\beta$ -ethyl- $\delta$ -phenyl- $\gamma$ -butene- $\alpha$ -carboxylic acid. *Macleod*..... 347

## 16 IV.

- $C_{16}H_{17}O_2N_3S$ . Ethyl ester of  $\alpha,\beta$ -diphenylthiourea- $\alpha$ -[aminocarboxylic acid] (3-thio-1-carbethoxy-2,4-diphenylsemicarbazide) *Nirdlinger* and *Acree*..... 236



**C<sub>17</sub>-GROUP.****17 II.**

C <sub>17</sub> H <sub>16</sub> O <sub>2</sub> . $\gamma$ -Keto- $\alpha$ -ethoxy- $\alpha,\gamma$ -diphenyl- $\alpha$ -propene ( $\beta$ - ethoxy - benzalacetophenone). <i>Reynolds</i> .....	323
C <sub>17</sub> H <sub>20</sub> O <sub>2</sub> . $\alpha$ - Hydroxy - $\gamma$ - ethoxy - $\alpha,\alpha$ - diphenylpropane (ethoxyethyldiphenylcarbinol). <i>Reynolds</i> .....	322

**C<sub>18</sub>-GROUP.****18 II.**

C <sub>18</sub> H <sub>18</sub> O <sub>4</sub> . Monoethyl ester of $\beta,\beta$ -diphenylethane- $\alpha,\alpha$ -dicarboxylic acid. <i>K. Reynolds</i> .....	320
C <sub>18</sub> H <sub>20</sub> O. $\alpha$ - Keto - $\beta$ - methyl - $\alpha,\gamma$ - diphenylpentane (ethyl - phenylisobutyrophenone). <i>Reynolds</i> .....	318
C <sub>18</sub> H <sub>36</sub> O <sub>2</sub> . Heptadecane- $\alpha$ -carboxylic acid (stearic acid). <i>Dakin</i> .	47

**18 III.**

C <sub>18</sub> H <sub>14</sub> O <sub>2</sub> N <sub>4</sub> . 2,6-Di[phenylazo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	20
C <sub>18</sub> H <sub>21</sub> ON. $\alpha$ -Oximido- $\beta$ -methyl- $\alpha,\gamma$ -diphenylpentane. <i>Reynolds</i> .	319

**C<sub>19</sub>-GROUP.****19 I.**

C <sub>19</sub> H <sub>20</sub> . $\gamma,\epsilon$ -Diphenyl- $\beta,\delta$ -heptadiene. <i>Reynolds</i> .....	328
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**19 II.**

C <sub>19</sub> H <sub>22</sub> O <sub>2</sub> . (1) $\alpha$ -Keto- $\gamma$ -ethoxy- $\alpha,\gamma$ -diphenylpentane. <i>Reynolds</i> .	326
(2) $\gamma$ -Hydroxy- $\alpha$ -ethoxy- $\alpha,\gamma$ -diphenyl- $\alpha$ -pentane. <i>Reynolds</i> .	326

**19 III.**

C <sub>19</sub> H <sub>14</sub> O <sub>2</sub> N <sub>4</sub> . 4 - Phenylazo - 5 - keto - 1 - phenyl - 3 - [2 - furyl] - 4,5-dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	420
C <sub>19</sub> H <sub>24</sub> O <sub>2</sub> N <sub>6</sub> . $\alpha$ -Semicarbazone- $\gamma$ -semicarbazine - $\alpha,\gamma$ - diphenyl - pentane. <i>Reynolds</i> .....	327

**C<sub>20</sub>-GROUP.****20 III.**

C <sub>20</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> . 5 - Keto - 1 - phenyl - 4 - benzyldiene - 3 - [2 - furyl] - 4,5-dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	419
C <sub>20</sub> H <sub>14</sub> O <sub>2</sub> N <sub>2</sub> . Phenylcarboxylate of 5 - hydroxy - 1 - phenyl - 3 - [2-furyl]-1,2-diazole. <i>Torrey and Zanetti</i> .....	418
C <sub>20</sub> H <sub>18</sub> O <sub>2</sub> N <sub>4</sub> . (1) 2,6-Di-[2-methylphenyl-1-azo] - 1,3 - dihydroxybenzene. <i>Orndorff and Ray</i> .....	34
(2) 4,6-Di-[2 - methylphenyl-1-azo] - 1,3 - dihydroxybenzene. <i>Orndorff and Ray</i> .....	33
(3) 2,6 - Di - [4 - methylphenyl - 1 - azo] - 1,3 - dihydroxybenzene. <i>Orndorff and Ray</i> .....	30
(4) 4,6 - Di - [4 - methylphenyl - 1 - azo] - 1,3 - dihydroxybenzene. <i>Orndorff and Ray</i> .....	27

$C_{20}H_{10}O_2N$ . Ethyl ester of $\alpha$ -cyan- $\beta,\delta$ -diphenyl- $\gamma$ -butene- $\alpha$ -carboxylic acid. <i>Macleod</i> .....	349
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**C<sub>18</sub>-GROUP.****22 III.**

$C_{22}H_{18}O_2N_4$ . (1) Diacetate of 1,3-dihydroxy-2,6-di[phenylazo]benzene. <i>Orndorff and Ray</i> .....	20
(2) Diacetate of 4,6-di[phenylazo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	17

**C<sub>23</sub>-ORROUP.****23 II.**

$C_{22}H_{22}O_2$ . $\gamma$ -Hydroxy- $\alpha$ -ethoxy- $\alpha,\gamma,\gamma$ -triphenyl- $\alpha$ -propene (ethoxytriphenylallyl alcohol). <i>Reynolds</i> .....	330
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**23 III.**

$C_{24}H_{16}O_2N_4$ . 4-[Naphthyl-2-azo]-5-keto-1-phenyl-3-[2-furyl]-4,5-dihydro-1,2-diazole. <i>Torrey and Zanetti</i> .....	421
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**C<sub>24</sub>-GROUP.****24 II.**

$C_{24}H_{24}O_4$ . 1,3-Diphenyl-R-butane-2,4-di[ $\beta$ -butene- $\gamma$ -carboxylic acid]. <i>Macleod</i> .....	344
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**24 III.**

$C_{24}H_{18}O_2N_6$ . 2,4,6-Tri-[phenylazo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	10
$C_{24}H_{22}O_4N_4$ . (1) Diacetate of 2,6-di-[2-methylphenyl-1-azo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	35
(2) Diacetate of 4,6-di-[2-methylphenyl-1-azo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	34
(3) Diacetate of 2,6-di-[4-methylphenyl-1-azo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	31
(4) Diacetate of 4,6-di-[4-methylphenyl-1-azo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	29

**C<sub>26</sub>-GROUP.****26 II.**

$C_{26}H_{28}O_4$ . Dimethyl ester of 1,3-diphenyl-R-butane-2,4-di[ $\beta$ -butene- $\gamma$ -carboxylic acid]. <i>Macleod</i> .....	345
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**26 III.**

$C_{26}H_{18}O_2N_4$ . 2,6-Di[naphthyl-1-azo]-1,3-dihydroxybenzene. <i>Orndorff and Ray</i> .....	38
$C_{26}H_{28}O_4Br_4$ . Dimethyl ester of 1,3-diphenyl-R-butane-2,4-di[ $\beta,\gamma$ -dibromopropane- $\gamma$ -carboxylic acid]. <i>Macleod</i> .....	345

**C<sub>27</sub>-GROUP.****27 II.**

- $C_{27}H_{16}O_2$ .  $\gamma$ -Keto- $\alpha$ -phenyl -  $\gamma$  - [4 - phenoxyphenyl] -  $\alpha$  - propene. (benzal -  $p$  - phenoxyacetophenone). *Kohler, Heritage and Burnley*. . . . . 68
- $C_{27}H_{22}O_2$ .  $\gamma$  - Keto -  $\alpha, \alpha$  - diphenyl -  $\gamma$  - [4 - phenoxyphenyl]propane ( $\beta, \beta$ -diphenyl -  $p$  - phenoxypropiofenone). *Kohler, Heritage and Burnley*. . . . . 68

**27 III.**

- $C_{27}H_{20}O_2Br_2$ .  $\gamma$ -Keto -  $\alpha$  - brom -  $\beta, \beta$  - diphenyl -  $\gamma$  - {4 - [4(?) - bromphenoxy]phenyl} propane. *Kohler, Heritage and Burnley*. . . . . 69
- $C_{27}H_{21}O_2Br$ .  $\gamma$  - Keto -  $\alpha$  - brom -  $\beta, \beta$  - diphenyl -  $\gamma$  - [4 - phenoxy - phenyl]propane. *Kohler, Heritage and Burnley*. . . . . 69
- $C_{27}H_{24}O_2N_6$ . (1) 2,4,6 - Tri - [2 - methylphenyl - 1 - azo] - 1,3 - dihydroxybenzene. *Orndorff and Ray*. . . . . 31
- (2) 2,4,6-Tri-[4-methylphenyl-1-azo] -1,3- dihydroxybenzene. *Orndorff and Ray*. . . . . 26

**C<sub>28</sub>-GROUP.****28 III.**

- $C_{28}H_{22}O_4N_6$ . Diacetate of 2,4,6-tri[phenylazo]-1,3-dihydroxybenzene. *Orndorff and Ray*. . . . . 12

**C<sub>30</sub>-GROUP.****30 III.**

- $C_{30}H_{22}O_4N_4$ . Diacetate of 2,6-di[naphthyl-1-azo]-1,3-dihydroxybenzene. *Orndorff and Ray*. . . . . 39

**C<sub>31</sub>-GROUP.****31 III.**

- $C_{31}H_{28}O_4N_6$ . (1) Diacetate of 2,4,6-tri[2-methylphenyl-1-azo]-1,3-dihydroxybenzene. *Orndorff and Ray*. . . . . 32
- (2) Diacetate of 2,4,6-tri[4-methylphenyl-1-azo]-1,3-dihydroxybenzene. *Orndorff and Ray*. . . . . 27

**C<sub>34</sub>-GROUP.****34 II.**

- $C_{34}H_{32}O_3$ . Isomeric compounds from  $\gamma$ -keto- $\alpha$ -ethoxy- $\alpha, \gamma$ -diphenyl- $\alpha$ -propene and ethylmagnesium bromide. *Reynolds*. . . . . 327

**C<sub>35</sub>-GROUP.****35 III.**

- $C_{35}H_{31}O_2N$ .  $\beta$  - Cyan -  $\alpha$  - ethoxy -  $\alpha$  - [ $\alpha, \gamma$  - diphenyl -  $\beta$  - propenoxy]- $\gamma, \epsilon$ -diphenyl- $\alpha, \delta$ -pentadiene. *Macleod*. . . . . 351

**C<sub>30</sub>-GROUP.****36 II.**

- $C_{36}H_{27}N_{11}$ . 4-Di[phenylazophenyldiazo]aminoazobenzene. *Orndorff and Ray*..... 39

**36 III.**

- $C_{36}H_{24}O_2N_6$ . 2,4,6 - Tri[naphthyl- 1 - azo] - 1,3 - dihydroxybenzene. *Orndorff and Ray*..... 36

**C<sub>40</sub>-GROUP.****40 III.**

- $C_{40}H_{28}O_4N_6$ . Diacetate of 2,4,6-tri[naphthyl-1-azo]-1,3-dihydroxybenzene. *Orndorff and Ray*..... 37

**ERRATA.**

- ✓P. 39, l. 25, formula should be  $C_6H_2(OCOCH_3)_2(N_2C_{10}H_7)_2$ .  
 ✓P. 58, l. 3 (from the bottom), formula should be  $C_6H_8O_4N_2$ .  
 ✓P. 121, l. 8, formula should be  $C_{11}H_{15}O_2N$ .  
 ✓P. 122, l. 30 *et seq.*, 2-nitro-5-methylbenzoic acid and derivatives should be 2-nitro-3-methylbenzoic acid, etc. (see Wheeler and Hoffman, p. 507).  
 ✓P. 123, l. 23, formula should be  $C_8H_8O_3N_2$ .  
 ✓P. 123, l. 24, 15.38 should be 15.55.  
 ✓P. 137, l. 8, the formula should be  $C_7H_7O_2N_2I$ .  
 ✓P. 319, l. 21, the formula should be  $C_{18}H_{21}ON$ .  
 ✓P. 352, l. 11 *et seq.*,  $\omega$ -ketotetrahydrooxazoles should be  $\mu$ -ketotetrahydrooxazoles.  
 ✓P. 428, l. 30, formula should be  $C_{13}H_9O_2N_2SO_3H \cdot 1H_2O$ .









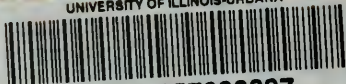








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